ECONOMIC GEOLOGY

VOL. XXIX NOVEMBER, 1934 No. 7

STRUCTURES AND TEXTURES OF SYNTHETIC REPLACEMENTS IN "OPEN SPACE."

C. SCHOUTEN.

CONTENTS.

Introduction 611
Experiments 613
Results obtained 615
Mascroscopic results 616
Structural and textural features 620
Replacements of individual minerals 621
Pyromorphite, cerussite, anglesite and phosgenite by galena 621
Smithsonite by sphalerite and galena 628
Sphalerite by argentite 630
Sphalerite or galena by chalcocite, covellite or galena 631
Pyrite and marcasite 634
Pyrrhotite 636
Sphalerite, galena, bornite, chalcocite and covellite by metallic silver or gold 638
Arsenides by metallic silver or gold 640
Chalcopyrite, bornite, covellite, chalcocite and cuprite 644
Gypsum by anglesite, with remarks on volume changes 650
Other replacements 652
Differing metal-displacements in various minerals by a one-salt solution 653
Summary and conclusions 654

INTRODUCTION.

SINCE the study of polished ore-sections has gradually become an important branch of investigation, much attention is drawn to the interpretation of textures and structures, but observers are

still far from agreement regarding this subject. Often one sees confirmation of his own theories in the textures and structures observed, but in most cases he can not be definitely sure of the correctness of his conclusions. It is often stated, without further explanation or on questionable grounds, that certain textures are "due to unmixing" or "indicate simultaneity" even where this is not at all certain. Examples of this sort are manifold in the literature. Up to the present, peremptory interpretations are not justified, and no satisfactory criteria can be formulated for possible modes of origin; a fact lately emphasized by Bastin *et al.*[1]

In intimate intergrowths of natural ore minerals the process of replacement is not easily recognized as such, with resulting doubt as to the origin. In synthetic replacements, on the other hand, metasome and palasome are definitely known and the process may be followed in all successive stages.

Some laboratory experiments on synthetic replacements were carried out by the writer about three years ago, with the hope of obtaining data on available criteria for replacements, based upon textures and structures observed in polished sections. The purpose of these experiments was neither to imitate replacements in nature, nor to draw conclusions with respect to the way in which they have been formed, but only to produce textures and structures that are due to replacement beyond any doubt. The positive and irrefutable data on metasomatic textures obtained by the experiments under discussion seem to support many of the views of Bastin *et al.* with regard to criteria of replacement textures.

The comprehensive literature existing on the subject, and the reproductions of textures and structures, are so widely scattered that it would occupy too much space even to cite them. German and American points of view are divergent. In part, the idea of the process known as "replacement" has become a question of "feeling," being very difficult to define with complete exactitude. Definitions have been given by Lindgren [2] and by Bastin.[3]

[1] Bastin, E. S., *et al.*: ECON. GEOL., vol. 26, pp. 561–610, 1931.
[2] Lindgren, W.: Bull. Geol. Soc. of Amer., vol. 36, pp. 247–261, 1925.
[3] Bastin, *et al.*: *Op. cit.*

Some experiments made by Ray,[4] C. F. Park,[5] Newhouse,[6] and by Young and Moore [7] have produced synthetic replacement textures, although on a small scale.

EXPERIMENTS.

More than 250 experiments were carried out, and over 150 photographs were taken. It is beyond the scope of this article to describe all these experiments, or to show all the photographs; only the most interesting will be presented.

Polished specimens of pure crystals, crystal-aggregates or mineral aggregates were studied, and eventually photographed, before and after the action of the solution.

In concentrated solutions the results obtained were astonishing, first, concerning the rapidity with which replacement may proceed under special and favorable conditions and, second, with regard to the solidity of the newly formed compounds. The experiments showed clearly that, at the surface of the polished section, all successive stages of replacement were obliterated in a "one-mineral" specimen. After etching, it was now and then obvious that texture and internal structure of the metasome were inherited from the host mineral.

Valuable textures, however, as might be suspected, can be observed only in the transitional zones, where replacement appears in both its initial and somewhat advanced stages. Hence, the specimen must be reground and repolished several times until, ultimately, even the initial stages in the center are obliterated.

The solutions were selected so as to preclude any doubt concerning the real metasomatic character of the process. Usually, either the acid or basic part was substituted, sometimes both, although in two stages. Only in few cases, were the acid and basic part substituted in one single stage.

The solutions were always aqueous, mostly concentrated, and

[4] Ray, J. C.: Econ. Geol., vol. 25, p. 433, 1930.
[5] Park, C. F.: Econ. Geol., vol. 26, p. 857, 1931.
[6] Newhouse, W. H. in Fairbanks: Laboratory Investigation of Ores, p. 161.
[7] Young, S. W., and Moore, N. P.: Econ. Geol., pp. 349–365; 574–581, 1916.

sometimes of odd and fantastic composition; a feature requiring further explanation.

Most observers, for their experiments, have made use of very dilute solutions, thus trying to imitate nature as much as possible. Such experiments, however, require much time, and even then, it is always open to question whether one can really compare synthetic experiments with processes in nature, if they do not simulate geologic conditions in every respect; a fact emphasized by Boydell.[8]

The experiments under discussion were mostly carried out in concentrated solutions, to hasten the results, and to produce deep replacements suitable to demonstrate the process from its initial stage to completeness. The selectivity of the process, however, may be seriously affected, for it is a well established fact that the attack upon different minerals generally becomes more selective in proportion as the solutions are more dilute.

From the above, it is clear, that *not the imitation of natural processes, but the produced textures and structures were the main object.* And, *reversely, these textures and structures possibly may occur in natural specimens also.*

Experiments were carried out in pyrex glass vessels closed with a ground and greased stopper, clamped to the vessel with two springs, in order to avoid the entrance of air. The springs were fixed to two bent projecting parts of both vessel and stopper. The vessels must be opened at the highest temperature reached before cooling.

Quantitative analyses were not made; hence the final chemical results can not be considered too much in detail. Metal-ions or acid-radicals, resulting from dissolution of the host, usually were confirmed in the solution.

Time required for replacement up to a depth of ¼ to 3 mm., varied from 1 hour to 48 hours, presupposing favorable conditions.

No attempts were made to consider whether the replacements were the results of molecular or colloidal solutions. Taking into

[8] Boydell, H. C.: Econ. Geol., vol. 21, p. 3, 1926.

account the influence of all changeable factors, every replacement in itself would be a field of investigation. This necessitated confining the experiments to a concise field. Therefore, pressure was always kept at about 1 atmosphere, whereas the temperature was not usually raised above 100° C.

All photographs illustrated were taken from artificial replacements.

RESULTS OBTAINED.

The following replacements were effected:

(*a*) Excellent: anglesite, cerussite, pyromorphite and phosgenite, by galena. Moderate or less good: marcasite, sphalerite, pyrite, siderite and smithsonite, by galena.

(*b*) Very good: sphalerite, galena, chalcocite and bornite by argentite, and chalcocite, by stromeyerite.

(*c*) Very good: galena, sphalerite, smaltite, chloantite, rammelsbergite, niccolite, safflorite, chalcocite, argentite and cuprite, by metallic silver. Moderate: chalcopyrite, bornite, siderite and covellite, by metallic silver.

(*d*) Excellent: sphalerite, galena, chalcopyrite, marcasite, bornite and covellite, by chalcocite. Moderate: pyrite, arsenopyrite, malachite, by chalcocite.

(*e*) Very good: bornite and chalcocite, by covellite. Moderate: galena, by covellite. Less good: sphalerite, by covellite.

(*f*) Good: marcasite, pyrite and pyrrhotite, by bornite or (and) chalcopyrite. Moderate: chalcopyrite, covellite, chalcocite, and enargite, by bornite or (and) chalcopyrite. Less good: galena and siderite. by bornite or (and) chalcopyrite.

(*g*) Excellent: cuprite, by metallic copper. Less good: siderite, by metallic copper and limonite.

(*h*) Moderate: siderite, by metallic lead.

(*i*) Excellent: marcasite, siderite and pyrite, by limonite.

(*j*) Excellent: several arsenides, carbonates, chalcocite, sphalerite, by metallic gold. Moderate: bornite, argentite, galena and pyrrhotite, by metallic gold.

(*k*) Moderate: galena, by anglesite.

(*l*) Moderate: pyrite, marcasite and arsenopyrite, by cuprite or (and) chalcocite.

(*m*) Moderate: covellite simultaneously, by chalcopyrite, bornite and pyrite.

(*n*) Excellent: sphalerite, chalcocite, covellite and chalcopyrite, by unknown silver compounds. Moderate: covellite and chalcopyrite, by unknown Cu-Sb-S-compound.

The depth of replacement often reached 1–5 mm., sometimes ¼–1 mm., whereas, in a few cases, only a very thin shell of ⅕ mm. or less had been formed.

Macroscopic Results.—Part of the artificial replacements could be observed quite well with the naked eye. (See Figs. 1–4).

One of the first experiments—reflecting the sulphidizing effect of sulphur compounds in flotation—had in view the action of a dilute K_2S-solution at room temperature upon a polished specimen of pyromorphite. The progress being relatively slow, the experiment was repeated with a concentrated K_2S_x-solution at 85° C. In a few minutes the pyromorphite was superficially altered to black PbS. When the section was removed, after 48 hours, it was observed that the external form and even the pits and furrows on the unpolished crystal faces had been excellently preserved. Except for its change in color, the aggregate seemed to be absolutely unmodified.

After repolishing, it was evident, on examination with the reflecting microscope, that the surface was entirely composed of PbS, free from any pyromorphite remnants. Again and again, the section was reground, repolished and re-examined. Figs. 1 to 3 show four stages of this replacement.

A striking observation concerning synthetic replacement of pyromorphite and phosgenite by galena was made, several times, when two different solutions were used consecutively. If a specimen has been immersed for two days in a K_2S_x-solution, and next for two weeks in a basic H_2S-solution, the outer shell of the specimen commonly shows only partial replacement (or perhaps an intergrowth of galena with an unknown compound) whereas the inner shell is composed of pure galena. This feature is well demonstrated in Fig. 3. A chemical explanation for this phenomenon can not be given at this time. By replacement in a K_2S_x-solution, or a H_2S-solution alone, only one shell of galena is formed; a combined solution of both, however, sometimes

yields the same phenomenon. Since both minerals contain $PbCl_2$ in their molecule, it is not impossible that this phenomenon is influenced by the hydrochloric acid set free by the reaction between $PbCl_2$ and H_2S.

It was observed that small cracks, originally present in the host, are often preserved. This proves the possibility that open fractures are *not always* younger than the minerals they traverse at the moment; a fact already suggested by Graton and McLaughlin[9] and recently mentioned by Graton and Davidson.[10]

Another fine example of macroscopic replacement, though chemically more complicated, is shown in Fig. 4. A polished specimen of "purplish brown" bornite, free from covellite and nearly free from chalcopyrite, was placed for 48 hours in a concentrated solution of $3FeSO_4.Fe_2(SO_4)_3$ at 85° C. After the action, the section seemed to be only slightly altered: the color had changed from purplish brown to yellowish brown, and many small cracks, not unlike "shrinkage cracks," were observed. After repolishing, the whole surface only exhibited "yellowish brown" bornite (?), resembling the well-known color and texture resulting from etching of bornite with nitric acid. When two millimeters were ground off, the center, composed again of unaltered original bornite, was bordered by two shells of different color (Fig. 4); the inner shell consisting of covellite, the outer shell of newly formed "yellowish brown bornite." This experiment is described in detail on another page.

From an aggregate of different minerals, one mineral is generally replaced exclusively or at least more readily than others. Examples of this kind of selective replacement were manifold, and showed clearly the fact, not sufficiently emphasized, that several successive, nearly complete, replacements may—and often do—produce textures closely simulating single replacements. Consequently, to the term "mineral A replaces mineral B," often mentioned in literature, the reader must usually add "or one or more minerals which had already replaced mineral B."

[9] Graton, L. C., and McLaughlin, D. H.: ECON. GEOL., vol. 13, pp. 81–99, 1918.
[10] Graton, L. C., and Davidson, S. C.: ECON. GEOL., vol. 23, pp. 158–184, 1928.

Synthetic and selective replacements may plainly accentuate textures and structures. This intensification of the contrasts in special cases may be a very applicable expedient for distinguishing between valuable carbonates, sulphates, phosphates of heavy metals and worthless gangue, such as: dolomite, calcite, siderite, barite, quartz, etc. In most cases it is difficult to discriminate these indistinct textures in consequence of the faint differences in color or reflective power.

Macroscopic, seemingly "centrifugal" replacement was observed by the use of "barrels" of pyromorphite. After grinding down about 1½ mm. in the direction of the longest axis of the "barrels," it was noted that their center was much more readily replaced than the outer shell. And, in reality, if the outer shell is by far the most resistant to the solutions, the term "centrifu-

---

FIG. 1. Pyromorphite crystals almost completely replaced by galena (white), showing preserved structure of crystal zones. (1 mm. ground off.) × 1¼.

FIG. 2. Less advanced stage, similar replacement of crystal aggregate (1 ½mm. removed). Note unsupported residuals. Galena, white; pyromorphite, gray. × 1¼.

FIG. 3. Another specimen, with 2½ mm. ground off, showing unaltered pyromorphite enveloped by galena (white). × 1¼.

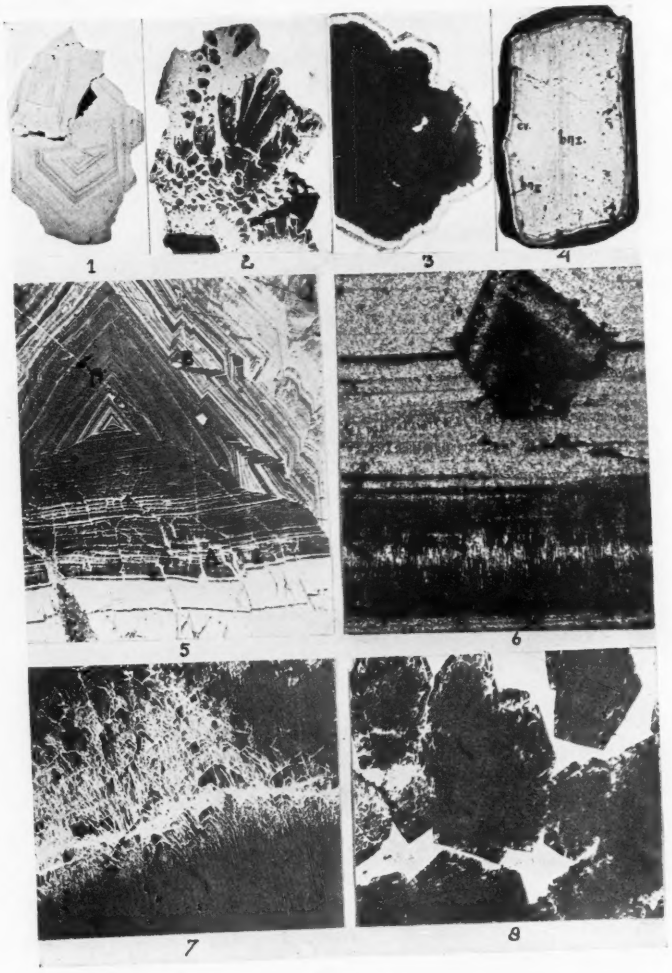
FIG. 4. Purplish brown bornite (*bn* I) replaced by covellite (*cv*) and yellowish brown bornite (?) (*bn* II). × 1¼.

FIG. 5. Selective replacement of certain crystal-zones of pyromorphite (gray) by galena (white). At *A* galena appears younger; but at *B*, pyromorphite apparently cuts galena. (1½ mm. beneath surface). × 23.

FIG. 6. Similar to Fig. 5, transmitted light, showing preservation of pyromorphite (white) structure in detail. Galena fibers (black) are arranged vertically to the crystal zones. × 60.

FIG. 7. Replacement of pyromorphite (gray) by galena (white). The solutions were guided by minute cracks and grain boundaries, originally invisible at highest magnification. × 190.

FIG. 8. Idiomorphic pyromorphite crystals (gray), exhibiting only faint alteration, whereas the interstitial fine-grained pyromorphite has been completely replaced by galena (white). × 115.



FIGS. 1–8.

gal" replacement—first mentioned by Hurst,[11] I believe, although Posepny [12] in 1893 suggested this possibility—would be justified.

The number of examples macroscopically visible could be greatly enlarged; several of the microscopic textures discussed in subsequent sections on a larger scale may be observed also with the naked eye or with a pocket lens.

STRUCTURAL AND TEXTURAL FEATURES.

Locke [13] and Whitman [14] draw attention to the fact that metasomatism has to be regarded as a process more physical than chemical in nature. It may be accepted that replacement is mainly governed by the *planes of weakness* in physical and chemical respects. The host-guest contact (or the front of replacement) owes its form first, to the physical and secondly, to the chemical planes of weakness. This applies not only to large and small structural field relations but also to textures of polished sections. Under the microscope, however, the internal structure of crystals or grains may be seen to greatly influence replacement structures.

Terms such as "islands," "embayments," "tongues" and "mainland," often used in discussions on metasomatism, indicate a certain similarity between coast-lines and the front of replacement.

This similarity may be illustrated by one of the synthetic examples. A radiated marcasite, after partial replacement, mainly shows three different textures, depending upon the directions in which the marcasite is cut. The section at right angles to the sheafs will show disconnected and irregular islands of marcasite in a matrix of limonite. A section in the direction lengthwise of the sheafs will exhibit two different textures. These three textures, respectively, may be compared with coastlines (*a*) where the mountains are isolated, (*b*) where mountain-ranges are at right angles to the coast, (*c*) where they are arranged parallel

[11] Hurst, M. E.: ECON. GEOL., vol. 17, p. 694, 1922.
[12] Posepny, F.: Trans. Amer. Inst. Min. Eng., vol. 22, pp. 197–369, 1893.
[13] Locke, A.: ECON. GEOL., vol. 23, pp. 93–98, 1928.
[14] Whitman, A. R.: ECON. GEOL., vol. 24, pp. 330–335, 1929.

to the coast. A specimen of marcasite partly replaced by limonite was ground and polished in the above-mentioned directions, and proved clearly this point of view.

It may be postulated that metasomatism shows a certain preference to proceed continually and more readily at those points or planes where it first started, and certainly the commencement is at points of weakness. The mineral mass in the neighborhood either is reached with difficulty, or is more resistant to the solutions. Irving [15] pointed out that the guest must generally have a porous texture at the moment of formation, and Boydell [16] also emphasized this fact at length. The penetrating solution, or at least the ions of a molecular solution, move easily to and from the front of replacement through the mass of the newly formed metasome; a feature experimentally supported, at low pressure and temperature, by the experiments under discussion. Hence, a regular diffusion-current being called into existence by the withdrawal of ions or molecules at the site of action, the prosecution of the process, commonly at the same points, is probable.

REPLACEMENTS OF INDIVIDUAL MINERALS.

Pyromorphite, Cerussite, Phosgenite and Anglesite Replaced by Galena.

Replacement of these oxidized products by galena is rarely to be found in nature. The great difference in reflective power of host and guest, however, produces structures and textures—the main object of this article—of such uncommon sharpness that it is desirable to reproduce them, because the same structures were also observed in replacements of other more common minerals.

All alterations of these oxidized products by galena were obtained at a temperature of 80°–85° C. Concentrated solutions of $K_2S_x + H_2S$, or of K_2S_x alone, proved to be the most favorable medium.

Irregular marginal relations between host and guest, with embayments, tongues, so-called "caries," ragged, impaired or

[15] Irving, J. D.: ECON. GEOL., vol. 6, pp. 527–561, 619–669, 1911.
[16] Boydell, H. C.: ECON. GEOL., *Op. cit.*, pp. 1–55.

undulating lines, are the most common. Several times—especially by cerussite—" pipes " or " channels " and tongues of galena were observed. Along fractures, occasionally, innumerable dots of galena were found, diminishing in quantity and size with distance from the fracture.

Fig. 5 shows a delicate zonal replacement-structure. Moreover, it demonstrates that errors concerning the diversity in age are not always precluded, and that this method of " etching " in some cases should not be disregarded.

The preparation of polished thin-sections permits examination of the same spot with both reflected and transmitted light. Selective replacement of certain crystal zones is shown by transmitted light in Fig. 6.

The walls of true replacement-fissures commonly were smooth and absolutely sharp, without ragged or impaired outlines; the walls even seemed to " match " completely.

The ability of solutions to penetrate the finest submicroscopic channels is demonstrated in Fig. 7. On the same grounds replacement may proceed preferentially along heterogeneous contacts. Among synthetic replacements, it was a common feature that all inclusions of quartz, calcite or dolomite, after the experiment, were bordered by uninterrupted rims of galena, whereas at some distance the cerussite was unaltered.

Finer grained material is commonly more readily replaced than coarser grained material of the same composition. Fig. 8 shows that in the small fracture-fillings of galena in the idiomorphic pyromorphite " remnants," the galena unmistakably must be the younger and replacing mineral. Upon further grinding down ½ mm., these crystals appeared to be completely unattacked; the interstitial material was still replaced. Thus, in a natural intergrowth of unknown minerals, *A* (idiomorphic and coarse) and *B*, exhibiting this last-mentioned structure, it will be difficult or impossible to unravel this simple structure with certainty. The completely sharp and unimpaired crystal faces of *A* would be considered by most observers to indicate that mineral *B* is either a filling of interstices, or has replaced another mineral that formerly occupied these interstices.

Replacement remnants may assume forms that are difficult of interpretation. In a few cases, it was shown that these remnants may imitate closely filled fissures. The possibility is not excluded, however, that these remnants originally were real fissures, filled with the same mineral, although less attackable by solutions. Similar textures in natural specimens might possibly cause a wrong interpretation.

Two or more minerals with similar chemical composition may be altered simultaneously by one solution; commonly, however, the replacement will be selective. An experimental proof of this feature is shown in Fig. 9, which demonstrates (1), that visible loss of volume in these pseudomorphs is not detectable, and (2), that the cerussite has sharp contacts with the galena, in spite of the fact that the cerussite at a level about ½ mm. higher had been replaced absolutely.

So-called intimate intergrowths and mutual boundaries have often been interpreted as positive evidence of simultaneous deposition, but Newhouse [17] pointed out their questionable validity as criteria for contemporaneous deposition, and Bastin *et al.*[18] stated that "they are not safe evidence of contemporaneity." Among synthetic replacements these textures are comparatively common, and often offer confirmatory evidence of replacement by the presence of many caries in the remnants. The intimate intergrowth shown in Fig. 10 suggests somewhat the possibility of simultaneity, or even of the reverse sequence. It is a striking feature that fissures, tongues, and filling along cleavage planes or other crystallographic directions are almost always absent in this kind of texture.

There exists similarity by selective replacement of limestone layers in the field, and of bands or layers in polished sections, and often it seems impossible to determine the finer causes influencing this selectivity. A section of pyromorphite examined under the reflecting microscope, showed nothing in particular except some cracks or small fissures. After treatment, the section showed banding and certain small layers were obviously

[17] Newhouse, W. H.: ECON. GEOL., vol. 23, pp. 647–659, 1928.
[18] *Op. cit.*

FIG. 9. Galena (white) pseudomorphic after pyromorphite, embedded in nearly unattacked cerussite. showing selective replacement. Note sharp edges of pseudomorphs. × 56.

FIG. 10. Remnants of cerussite (gray) in galena (white). Texture approaching so-called mutual boundaries. × 56.

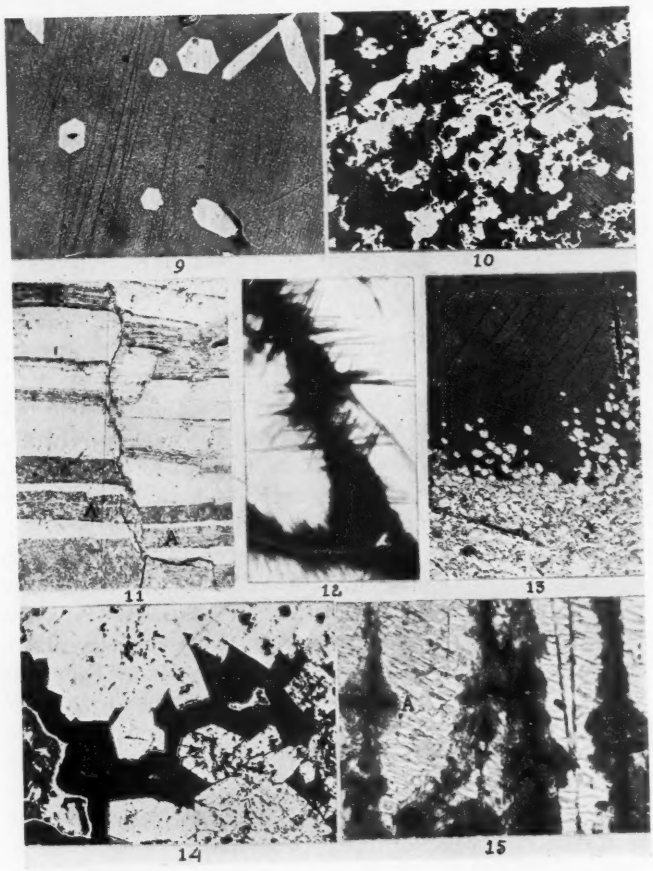
FIG. 11. Replacement of bedded pyromorphite (gray) by galena (white). The fault and the open fissure, both existing originally, only *appear* to be younger than galena. The fault, however, may be even older than pyromorphite, *viz.:* if pyromorphite had already replaced another faulted mineral. × 42.

FIG. 12. Fine needles of galena (black) projecting as guest into cerussite (white); replacement proceeding outward from a minute fissure. Transm. light, × 315.

FIG. 13. Replacement of a pure phosgenite crystal (gray) with distinct cleavages by galena (white), from near border of specimen, after grinding off 2 mm. Irregular and globular replacement without visible relationship to host structure. Note isolated galena islands, the initial replacement along an elongated quartz grain (left), and the reaction-rims (dark gray) of unknown composition between phosgenite and galena. × 35.

FIG. 14. Galena (white) has completely replaced original or pseudomorphic cerussite. Dark gray—siderite; gray rims between galena and siderite—limonite. × 105.

FIG. 15. Replacement of smithsonite (white) by sphalerite (gray) and of this in its turn by galena (black). Cruciform galena figures at *A*, dendritic forms at *B* and *C*. The cross of galena (*A*) seems to have no relation to the cleavage directions of smithsonite; the longest beam of the cross, however, parallels the smithsonite fibers. In detail (not clearly visible in illustration) the two lower edges of the galena at *D* are parallel to the cleavage directions of the smithsonite.



FIGS. 9–15.

more resistant to solution than others. The texture produced (Fig. 11) offers safe evidence of the pre-existence of a small fault-fissure and of a minute open crack. Even in the middle of the faulted layer *A*, a very thin layer of galena, (about 0.006 mm. thick) may be observed, clearly demonstrating the sensitiveness of the process regarding variations in granularity, porosity or chemical composition. It may be noted (Fig. 11), that the fault plane does not match completely with the fracture traversing the layers. In a natural texture of this kind, the wrong interpretation that the fault, and certainly the open fracture, developed subsequent to the deposition of both minerals, is not excluded. It was shown that certain layers at one side only of the fault were replaced. In places, at irregular distances along an open fracture, small but plain " ore shoots " or enlargements of synthetic galena, having no visible relationship to the different layers or to the granularity, were formed.

The host-guest contact generally has ragged or impaired outlines (faintly visible in Fig. 3), but often it was observed that fissures or tongues were absent at the front of replacement, the contact plane being smooth and sharp. Advanced rounded islands of the host are in places separated from the mainland.

Fine needles of galena, penetrating along crystallographic planes of cerussite and proceeding outward from a narrow fracture, are shown in Fig. 12. This delicate synthetic structure in some degree resembles the well-known tourmaline needles along microscopic fissures in thin sections of cassiterite veins of Bolivia or Cornwall. In places, the center of a grain is completely spangled with minute disconnected rods in two or three directions, without visible connection to microscopic fissures or even to the outlines of the grains. Magnified 600 times, this structure simulates the well-known regular chalcopyrite rods in bornite, often attributed, and in some cases perhaps rightly, to unmixing.

Metasomatism may not show any relation to the crystal-structure of the host. The external form, roughly speaking, may be preserved, the internal structure may be wholly obliterated (Fig. 13). Notwithstanding the existence of these cleavages of the host (Fig. 13) and the fact that the replacing solutions

here especially penetrated the specimen from the upper part of the field, the rounded "inclusions" of galena have no visible connection with each other, nor with the mainland of the galena border. Some of these galena spots are not globular; in a few cases they assume a square form. It seems probable that these may be called small "metacrysts."

The succession of minerals may be exactly the reverse of that suggested at first sight. In Fig. 14 it seems obvious that the vug-filling (dark gray) is the last precipitated mineral. But in reality the white and apparently idiomorphic mineral (galena) has been formed as synthetic pseudomorphism after cerussite; hence it is the youngest mineral. The original polished section was composed of an aggregate of cerussite (probably already pseudomorphic) bordered by small rims of limonite; the interstices being filled with siderite. It is known that only a few ore minerals (mostly hard minerals) in compact ore assume their own form, *e.g.* pyrite, arsenopyrite, safflorite, magnetite and others. The softer minerals such as galena, chalcopyrite and silver compounds scarcely if ever do; they may crystallize idiomorphically in vugs. In compact ore, straight outlines of soft ore-minerals generally result from pseudomorphism or crystallographic planes of the bordering minerals. Straight outlines, then, have too often been recorded as the "idiomorphic form" or as "metacryst."

A specimen composed of calcite, for the greater part replaced by cerussite, was immersed in the K_2S_x solution for two days. After repolishing, the calcite inclusions were left wholly embedded in the synthetic galena, so that apparently it was the calcite that was replaced, instead of the cerussite. This observation affirms once more that several successive replacements may produce textures closely simulating single replacements. On the other hand, it may be pointed out that exactly these remnants embedded in the metasome may offer conclusive evidence of replacement, provided they are present as inclusions with similar outlines in the host.

Replacement textures produced on crystal faces commonly differ from those obtained on arbitrary polished surfaces. An unusual texture resulted from action of a solution of H_2S and

KOH for two days on a crystal face of pure, transparent, colorless cerussite. About 1 mm. beneath the surface a texture appeared suggesting simultaneous deposition and in many respects simulating certain natural graphic textures.

Alteration of oxidized lead compounds to galena without supply of newly precipitating galena should cause volume changes for pyromorphite-galena of about 20 per cent. A crystal of 12.5 mm. length and 6 mm. thickness, after nearly total alteration to galena, suffered no noticeable change in volume, not even after three weeks. Hence, the loss of volume resulted in porosity. After drying at 100° C. for two days, however, the specimen was found to have many cracks, not unlike "shrinkage" cracks, proving the loss of volume by contraction. The replacement-porosity before drying is often not detectable at the highest powers of the microscope.

Synthetic replacements produced in H_2S gas instead of in aqueous solutions yielded some peculiar results. After some time little drops of liquid "squeezed out" of the specimen, and in the long run prevented deeper attack. If the host was pyromorphite, these drops gave strong reactions for phosphoric and hydrochloric acid. The textures in many cases were similar to those obtained in solutions. In one of the specimens, minute rounded dots of galena were clearly arranged along two or three crystallographic directions of the palasome, closely simulating the well known inclusions of chalcopyrite in sphalerite, although they can not be directly compared with these. In reality, the natural inclusions have similar sections in all directions, whereas these synthetic galena dots must be considered as the terminations of minute conical replacement-channels.

The reverse replacement (galena by anglesite), produced in concentrated solutions of ferric sulphate with a trace of sulphuric acid, proceeded much more slowly.

Smithsonite Replaced by Sphalerite and Galena.

This replacement caused the formation of curious textures imitating well known, and often disputed, natural ones.

A polished section of pure, white and radiating smithsonite from Laurion (Greece) was placed for 48 hours in a K_2S_x solution at 80° C. After regrinding and repolishing, the smithsonite showed partial replacement by sphalerite, especially parallel to the smithsonite fibers. Next, the specimen was immersed for 24 hours in a concentrated solution of $Pb(OK)_2$ at 80° C. The reground and repolished section showed dentritic and cruciform figures of galena surrounded by elongated spots of sphalerite (Fig. 15). These textures in many respects resemble those of native silver or bismuth surrounded by arsenides from the cobalt-silver veins, or those of galena and sphalerite from Moresnet and Pribram, illustrated by Guild,[19] Van der Veen [20] and Schneiderhöhn.[21]

Probably this experiment supports in some respects the view of Van der Veen that dendritic and cruciform textures may be inherited from carbonates, although this may not necessarily be the case.

Here the occasion presents itself to decide what name should be given to the ultimate result. Suppose the smithsonite had been treated for 2 days with K_2S_x-solution, yielding sphalerite, and then for the next 6 days with a solution of $Pb(OK)_2$; then, all the sphalerite would have been replaced by galena, the ultimate texture apparently proving the direct replacement of smithsonite by galena. In reality this conclusion is not justified, as is conceded by many investigators in recent years.

A thorough study of successions in hypogene replacements (not only the age sequences) may afford evidence for a satisfactory explanation of many astonishing facts. It is desirable to avoid expressions such as " stephanite replaces quartz " simply because the quartz crystals have impaired outlines against the stephanite. These outlines may be the result of successive replacements, *e.g.* by carbonate, sphalerite, galena and stephanite. The ultimate result only seems to be direct replacement of quartz by stephanite.

[19] Guild, F. N.: Econ. Geol., vol. 12, pp. 297–353, 1917.

[20] Van der Veen, R. W.: Mineragraphy and Ore Deposition, Figs. 41, 109, 110.

[21] Schneiderhöhn, H.: Lehrbuch der Erzmikroskopie, Bd. II, Figs. 35, 257.

It may be stated that attempts were made to replace smithsonite by galena directly; the experiments were only partially successful. If smithsonite was placed in a solution of PbS_2O_3 dissolved in an excess of $Na_2S_2O_3$, the smithsonite was deeply attacked and a crust of galena, perhaps together with sulphur, was deposited. The newly formed material, however, was too soft to be polished.

Sphalerite Replaced by Argentite.

Sphalerite specimens were immersed in solutions of $AgNO_3$, $AgNO_2$, Ag_2SO_4 or Ag_2O, and were left for periods of a few hours to two days, at a temperature of 80° C. Curious phenomena and diverse replacements may be brought about if diffusion cases are used, changing the solutions and minerals or metals inside and (or) outside. The description of these results and the explanation of the—partly inconceivable—chemical reactions would occupy too much space here.

In general, the replacement of sphalerite by argentite develops irregular structures and textures resembling, for example, Figs. 2, 7 and 10.

A small fracture, only feebly visible at high magnification, may be enlarged by replacement to a real "brecciated or replacement" vein with unsupported fragments (Fig. 16). It is interesting to examine under the microscope different stages of enlargement of the fissure, reduction in size of the enclosed remnants, and mode of impairment of the walls. Rarely, the walls of a straight fracture were not "impaired" after enlargement up to one millimeter; the walls still matched.

Replacement along heterogeneous contacts is illustrated in Fig. 17. This texture closely resembles those of chalcocite replacing sphalerite in Tsumeb ores.

Preferential replacement of certain twinning lamellae of sphalerite is not common in nature, examples in the literature being rare. Synthetic examples were now and then obtained, as follows:—Two polished sections—one composed of galena, the other of sphalerite—were laid one upon the other, with the surfaces isolated by three sheets of filter paper; the whole was immersed in $AgNO_3$

solution. Replacement of sphalerite in that way proceeded much more readily than with sphalerite alone. This is probably due to the formation of an electric couple which may influence greatly the selectiveness and velocity of the process.

Fig. 18 is an example of a similar electrical phenomenon; a result obtained in some hours by use of a diffusion case. However, small rims of sphalerite commonly were left unattacked at the contact with galena or other minerals.

Sphalerite or Galena Replaced by Chalcocite, Covellite or Galena.

These experiments were carried out with several copper solutions, *e.g.* $CuSO_4$, $Cu(NO_3)_2$, $CuCl_2$, Cu_2Cl_2 and $Cu(OK)_2$, with or without addition of ferrous or (and) ferric sulphate. All these copper compounds brought about replacements of sphalerite or galena to a greater or less degree. Galena, of course, is not as readily replaced in $CuSO_4$ solution as in $Cu(NO_3)_2$ solution, since in the former case two insoluble compounds are formed. The quickest replacements were produced with a $Cu(OK)_2$ solution in KOH at higher temperature (120°–130° C.). Generally irregular textures were obtained, remnants with convex curved outlines being common.

Replacement of sphalerite in its initial stage often originates from small irregular fissures (Fig. 19). The ultimate textures of this figure closely resemble those of Tsumeb ores described by Schneiderhöhn.[22]

Chalcocite—as well as argentite—may also replace galena and sphalerite nearly exclusively along cleavage planes. Natural replacement of sphalerite by chalcopyrite or chalcocite sometimes causes the formation of fragments in the form of triangles or parallelograms, isolated from each other by the guest. Van der Veen has given a fine example of the initial stage.[23] The remnants of sphalerite even in an advanced stage are mostly relatively sharp (Fig. 21), whereas those of galena commonly are some-

[22] Schneiderhöhn, H.: Metall und Erz, 1920–1921. Die Erzlagerstätten des Otaviberglandes; also: Lehrbuch der Erzmikroskopie.

[23] *Op. cit.*

what irregular and rounded (Fig. 20). It may be emphasized that the replacement textures of galena sometimes show the negative design of Fig. 20, since the cleavage lines are bordered by a rim of unattacked galena. whereas the main mass is completely replaced.

In $Cu(OK)_2$ solution, galena is more readily replaced by covellite and chalcocite than is chalcopyrite. This is explicable, for the loss of volume by this replacement ($PbS + Cu(OK)_2 = CuS + Pb(OK)_2$) theoretically and apparently should be about 36 per cent, since $Pb(OK)_2$ is soluble in the excess of KOH. The action of a $Cu(OK)_2$ solution on chalcopyrite, however, may give rise to the formation of several insoluble compounds, such as Cu_2S, CuS, FeS, $Fe(OH)_2$, and $Fe(OH)_3$. Hence, theoretically, a considerable increase of volume, preventing the easy penetration of solutions, may be the result. This explanation will not always apply, as will be shown in a subsequent section.

FIG. 16. Unsupported fragments of sphalerite (gray) in a veinlet of argentite (light) replacing sphalerite. × 30. This indicates the similarity of synthetic and natural textures.

FIG. 17. Replacement of sphalerite (gray) by argentite (white), along both sides of a preëxisting carbonate veinlet (dark gray) and grain. × 30.

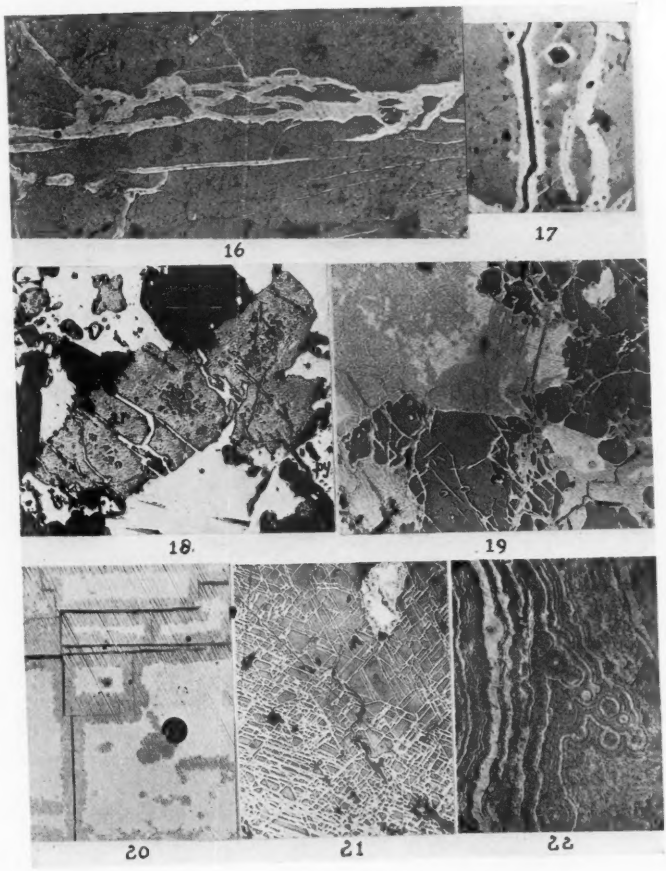
FIG. 18. Sphalerite (gray) selectively and nearly completely replaced by argentite (*ar*). Galena (white) is unaltered. Small sphalerite remnants (*sl*). The veinlet of galena traversing the argentite appears to be the youngest mineral; in reality the synthetic argentite is younger. *py*—pyrite; *qu*—quartz. × 70.

FIG. 19. Replacement of sphalerite (gray) and galena (white) by chalcocite (faint gray). The original sphalerite was nearly free from visible fractures. In a more advanced stage only remnants of sphalerite are left (at *A*). The galena is obviously more replaced than the sphalerite. × 70.

FIG. 20. Replacement of galena (white) along cleavage planes by chalcocite (gray). × 70.

FIG. 21. Sphalerite (gray) replaced by chalcocite (white) along cleavage planes. Galena above (white). × 46.

FIG. 22. Selective replacement of sphalerite-bands (var. schalenblende) by chalcocite (white). × 70.



FIGS. 16–22.

Fig. 22 demonstrates clearly the selective replacement of certain sphalerite layers from a specimen of "schalenblende" from Moresnet. The possibility of this kind of inherited structure has been already taken into account by Colony.[24]

Other results may be enumerated briefly, as follows:

A solution of $CuSO_4 + Fe_2(SO_4)_3$ etched the sphalerite deeply without replacement.

In a solution of $Fe_2(SO_4)_3 + CuSO_4 + FeSO_4$ sphalerite was slowly replaced by covellite with preservation of structure.

In a concentrated $CuSO_4$ solution with some H_2SO_4 the same result was obtained.

In a solution of PbS_2O_3 with $Na_2S_2O_3$ the sphalerite was feebly replaced by galena and was coated with sulphur. Certain twinning lamellae especially were selectively replaced.

In a solution of $CuSO_4 + FeSO_4$ galena seemed to be replaced by chalcocite with some covellite.

Pyrite and Marcasite.

The natural remnants of pyrite and marcasite, repeatedly illustrated by several authors, are so similar to those synthetically produced, that the reader examining photographs of the last-mentioned category would believe he was looking at natural textures. Only a few photographs will be described.

The textures and structures synthetically produced commonly depend upon those of the host. Consequently, they differ greatly for pyrite and marcasite.

Remnants of long-continued and irregular replacement of pyrite resemble the common textures of pyrite replaced by bornite, chalcocite, limonite or other minerals. Selective replacement of certain crystal zones may produce structures like that shown in Fig. 23. This zonal replacement—taken from a specimen composed of pure pyrite from Oruro, Bolivia—closely resembles the natural structures of pyrite and jamesonite sometimes observed in the same ore.

It may be emphasized that the crystal faces of pyrite are occasionally much more resistant than the center of the crystal.

[24] Colony, R. J.: Ore Mineral Sequences. In Fairbanks: Laboratory Investigations of Ores.

In that case elongated remnants with partially unmodified crystal outlines may remain.

A fine example of selective zonal replacement of pyrite by chalcocite is shown in Fig. 26, taken from a specimen composed of pyrite, melnikowite [25] and sphalerite (var. schalenblende) from Raibl. This structure closely resembles the natural zonal replacements, for example, of carbonates by silver halogenides,[26] or of nickel and cobalt arsenides by metallic bismuth.[27] In other parts of the same specimen textures of marcasite and melnikowite replacement closely similar to that shown in Fig. 22 were observed.

There is even more diversity in textures and structures of marcasite than of pyrite. This is conceivable considering the fact that pyrite commonly is granular in habit, whereas marcasite generally has a fibrous, reticulated, spear- or comb-structure. Pyrite sections, therefore, will be influenced only slightly by the direction in which the grains are cut, whereas marcasite will have at least three sections with different designs.

A texture that could result from marcasite as well as from pyrite is shown in Fig. 24, demonstrating synthetic replacement of marcasite by "limonite," produced in a concentrated solution of $KMnO_4$ with a trace of H_2SO_4. After etching, the well-known limonite structure, consisting of concentric layers, was delicately developed; it is faintly visible even in Fig. 24, taken before etching. Fig. 25 shows comb-like remnants of marcasite as a result of long continued replacement by chalcocite.

The most rapid replacements of pyrite and marcasite were produced in solutions of $Cu(OK)_2$ in KOH (for impure chalcocite) and of concentrated $KMnO_4$ with a trace of sulphuric acid (for "limonite"). Slower reactions were observed with dilute solutions of $CuSO_4 + FeSO_4$, or of concentrated $CuSO_4$ and $FeSO_4$. In the former case a porous soft and yellow coating was formed, closely resembling chalcopyrite after polishing; in the latter, pyrite and marcasite were replaced by impure chalcocite.

[25] First described by H. Ehrenberg. Neues Jahrb. f. Mineral., B. LVII, Abt. A, p. 1303; and Zeit. f. Krist., Bd. 66, pp. 478–480, 1928.

[26] Whitehead, W. L.: Econ. Geol., vol. 14, 1919, pp. 1–45.

[27] Van der Veen, R. W.: *Op. cit.*

In solutions of $Pb(OK)_2$ in KOH or in KNa-tartrate, pyrite and marcasite in a few hours were coated with galena. This coating was very thin but of extraordinary solidity and did not grow in thickness noticeably after some days' immersion; it remained in its initial stage. Probably the increase of volume causes the formation of galena of such compactness that it gradually prevents further penetration of the solutions.

Pyrite from Elba and from Colorado were only feebly attacked by the solutions, whereas pyrite from Rio Tinto and marcasite from Joplin were much more readily replaced.

Pyrrhotite.

In a solution of K_2S_x pyrrhotite apparently remains unaltered. Specimens treated with a solution of $Cu(OK)_2$ showed an intergrowth probably consisting of "limonite" and chalcocite.

In solutions of $FeSO_4$ and Cu_2Cl_2 the pyrrhotite swells and falls to pieces in consequence of the increase of volume. The fragments of one specimen were surrounded by sealing wax and

---

FIG. 23. Replacement of certain crystal zones of pyrite by blue chalcocite (gray). × 115.

FIG. 24. Marcasite (white) replaced by "limonite" (gray). × 23.

FIG. 25. Radiating or comb-like marcasite remnants (white) in chalcocite (gray). Chalcocite faintly etched. × 68.

FIG. 26. Selective replacement of certain crystal zones of pyrite (white) by chalcocite (gray). × 68.

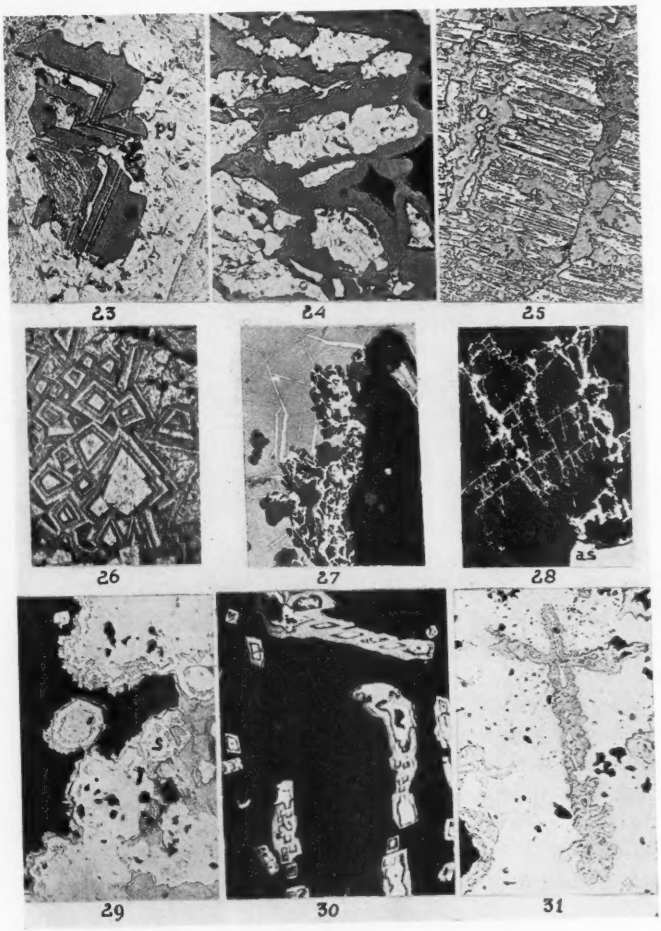
FIG. 27. Metallic silver (white) replaces sphalerite (gray) and galena (grayish white). In sphalerite the replacement is irregular, in galena it is guided by cleavage directions. Black—quartz. × 68.

FIG. 28. Replacement of carbonates (gray) by metallic gold (white) caused by the reaction between the gold solution and arsenides. Part of an arsenide grain (*as*) is visible. × 68.

FIG. 29. Arsenides (grayish white) almost completely replaced by metallic silver (*s*). Remnants of safflorite at the contacts of silver and gangue. × 68.

FIG. 30. Selective replacement of the kernels of arsenides (gray) by metallic gold (white). × 68.

FIG. 31. Smaltite and safflorite remnants (gray) in metallic silver (white) as metasome. × 68.



FIGS. 23–31.

were then polished. The pyrrhotite was replaced, along grain boundaries and cracks successively, by chalcopyrite, bornite and chalcocite. Pyrrhotite in a concentrated solution of $CuSO_4$ fell to pieces and was partially replaced by chalcocite and covellite.

Sphalerite, Galena, Bornite, Chalcocite and Covellite Replaced by Metallic Silver or Gold.

Sphalerite and galena in a $AgNO_3$ solution will generally be replaced by argentite. If, however, the specimen containing both sulphides is immersed in a diffusion case filled with this solution, the whole being placed in a glass-vessel containing a dilute solution of NH_4OH, the greater part of both minerals may be replaced by metallic silver. During these experiments specimens composed of much sphalerite and little galena fell to pieces, whereas those composed of much galena and little sphalerite remained intact.

In addition to replacement, filling of small open fractures and vugs also takes place, since the volume of precipitated silver is greater than that of the dissolved sphalerite or (and) galena. Both minerals concurrently are replaced by metallic silver, but the fissure fillings of galena enclosed in sphalerite are more readily replaced than each of the pure and isolated minerals (Fig. 27). The same specimen was again examined after retreatment in the same solution. It was then observed that the sphalerite was almost completely replaced, and the silver-laths in galena were visibly enlarged.

At greater depth beneath the original polished surface, the quantity of short argentite veinlets replacing galena along cleavage directions increases at the cost of metallic silver. If both metallic silver and argentite replace galena, the outlines of the remnants in argentite are commonly irregular, whereas those in silver are rectilinear and resemble closely natural textures of the same kind, such as those illustrated by Berg.[28]

The direct replacement of sphalerite by gold in a solution of $AuCl_3$ did not succeed at all, or at least not to any significant extent. However, no experiments were tried in diffusion cases.

[28] Berg, G.: Metall. u. Erz, Bd. 18, pp. 321–325, 1921.

Fine indirect replacements in two stages were induced, however, if sphalerite was first partially converted, into chalcocite, and this metasome into metallic gold.

It is well known that chalcocite is one of the strongest precipitants for silver and gold from solutions.[29] Hence, this mineral will be replaced readily by metallic silver or gold, provided that the penetration of the solutions is not prevented by the compactness of the precipitated metal. In these experiments, crustification and filling of open fissures and vugs were also observed. The replacement of chalcocite in a solution of $AgNO_3$ takes place in three stages, viz, chalcocite-stromeyerite-argentite-metallic silver. At the border of the specimen these four layers could be observed very clearly. The first layer of massive silver is a crustification, the others are true replacement layers. That part of the metallic silver that really replaces the chalcocite—or more exactly, the newly formed argentite—in its initial stage, surrounds all original rhombic chalcocite grains, thus apparently producing an exsolution-texture.

In a solution of $AuCl_3$, part of the chalcocite was converted into covellite, and part was replaced by gold. Concurrently with the replacement, open fissures were filled with or bordered by this metal. The textures produced seem to give safe evidence that fissure-fillings were younger than the covellite. This statement must be deemed worthy of further study, especially in view of supergene textures of silver and gold deposits.

As a rule, it is tacitly accepted that filled fissures are younger than the traversed minerals, and usually this is justified. However, let it be assumed that hypogene gold or silver fills a fissure in galena, sphalerite or chalcopyrite. Supergene solutions are able to replace these three sulphidic minerals by chalcocite or covellite. The ultimate texture apparently indicates that gold is the youngest mineral. Moreover, these experiments show that, if hypogene silver or gold solutions act on hypogene minerals, the possibility is not quite excluded, that these minerals may be replaced by others, and simultaneously gold or silver may be

[29] Palmer, C., and Bastin, E. S.: ECON. GEOL., vol. 8, pp. 140–170, 1913.

deposited in the original or newly formed microscopic fissures traversing these minerals. In that case fillings are of the same age as the metasomatic minerals they traverse.

In most cases, paragenetic relations, geological reasonings, comparisons in color of undoubtedly hypogene and supergene gold and silver in the same deposit, or etching tests, may give conclusive evidence.

Covellite was synthetically replaced by metallic silver in a diffusion case filled with concentrated silver solutions maintained at a temperature of 70° C., and in the transition zone an unknown silver compound, very faint purplish against chalcocite, was formed. Nitric acid tarnished this compound—probably stromeyerite—only feebly. The structures of covellite and this compound in many respects have some resemblance to those of stromeyerite illustrated by Guild.[30]

Bornite, in a solution of $AgNO_3$, is quickly coated with metallic silver. After 48 hours the bornite was deeply replaced by a grayish silver compound (probably argentite) together with metallic silver. This grayish white guest and the bornite locally show a graphic texture; in other parts of the same specimen this compound passes gradually to bornite without a visible transition zone.

Arsenides Replaced by Metallic Silver or Gold.

Upon etching niccolite with a silver-nitrate solution, a coating of metallic silver forms. The mineral niccolite is dissolved, and the silver simultaneously precipitated takes up the space formerly occupied by niccolite. Hence, for this kind of etching-test the use of the term " synthetic replacement of niccolite by silver " is amply justified. But the result may not be only a thin coating; replacements up to a depth of several millimeters may be produced in a few days.

The textures and structures developed by these experiments strikingly resemble those observed in nature, especially in the ores

[30] *Op. cit.*, pl. XII, XIII, pp. 344, 345.

of Cobalt (Ontario),[31] Schneeberg (Erzgebirge) [32] and Joachimstal (Bohemia).[33] Pure arsenides from these localities were used in the experiments.

To begin with, some figures will be discussed, and next, some hypothetical considerations will be taken up.

Irregular, zonal and concentric replacements, sometimes apparently centrifugal, are most commonly developed. Irregular replacements along small fractures often cause textures similar to those illustrated in Figs. 2, 16 and 24; zonal replacements develop structures similar to those of Figs. 23 and 26, whereas concentric replacements show certain similarity to Fig. 22.

An example of apparently centrifugal replacement is shown in Fig. 29. The outer shell (safflorite) is much more resistant to replacement than the center, originally composed of chloantite, smaltite and niccolite.

A noteworthy phenomenon is shown in Fig. 30, a specimen from Schneeberg (Germany) composed of arsenides inclosed in a matrix of quartz. After treatment with a solution of $AuCl_3$, superficially all arsenides were replaced by gold, but after grinding down about one-half millimeter it was observed that the kernels still were replaced, the rims being unaltered. This texture —as might be supposed—is really the same as the natural intergrowth of arsenides with native bismuth or other minerals of Schneeberg.

In Fig. 31, one of the arsenide remnants of Cobalt (Ontario) ore, after synthetic replacement of the arsenides by silver, is illustrated. The smaltite remnant in the center of the figure is cross-shaped; its center, in turn, is partially filled with silver. This texture constitutes one of many examples of the resemblance to natural intergrowths of Cobalt ores, and of selective replacement. From this specimen rammelsbergite and niccolite especially were more readily replaced than smaltite and safflorite.

[31] Bastin, E. S.: ECON. GEOL., vol. 12, 1917, Pls. VII and VIII (Bastin) and X (Guild).

[32] Guild, F. N.: ECON. GEOL., vol. 12, 1917, Pl. XVII, Fig. *A*, Pl. XVIII, Figs. *A* and *B*, Pl. XIX, Fig. *B*.

[33] Van der Veen, R. W.: *Op. cit.*, Figs. 77, 84, 86, 62.

That niccolite-calcite intergrowths in these ores were selectively replaced, was inferred by Schloszmacher.[34]

Of course it is not my intention to draw a parallel between these synthetic replacements and the origin of these ores in nature, for it is a matter of course that the textures and structures originally existing are not elucidated by these experiments; but metasomatism is able without doubt to preserve the textures that once existed. At least, this point of view supports, in some respects, the ideas of those who have ascribed an important rôle to metasomatism in the deposition of bismuth, silver or gold.

Moreover, not only were the arsenides replaced by gold or silver, but also the carbonate gangue. This was proved in the following way: A polished specimen composed of arsenides having—at a rough estimate—about 10 per cent of carbonate-gangue, was covered over half of its area with a film of wax and placed in a solution of $AuCl_3$. After regrinding and repolishing, all gangue, and the greater part of the arsenides, superficially was shown to be replaced by gold in the half of the specimen free from wax. The ultimate result near the polished surface was a complete replacement by gold; the transition zone showed gold with remnants of arsenides; all gangue was replaced. The initial stage of carbonate replacement is guided by cleavage planes, as is illustrated in Fig. 28. Pure carbonates of calcium and magnesium free from arsenides, however, are not replaced to any extent.

The physical and chemical explanation of this phenomenon is widely divergent from that by replacement of, for example, anglesite by galena, following the stoichiometric equation: $PbSO_4 + K_2S = PbS + K_2SO_4$.

The replacement of arsenide by metallic silver could take place according to the stoichiometric equation, supported by experimental data, by Palmer and Bastin:[35]

$$2NiAS + 5Ag_2SO_4 + 3H_2O = 2NiSO_4 + 3H_2SO_4 + As_2O_3 + 10Ag. \quad (1)$$

[34] Zeit. f. prakt. Geol., 1921, pp. 131–134.

[35] *Op. cit.*

Hence, the volume of the newly formed silver should be about three times that of the dissolved niccolite, an increase of 200 per cent. The greater number of the polished specimens after longer action swelled and fell to pieces, thus indicating a great increase of volume.

If the replacement of niccolite by silver progresses according to equation (1), the acid set free by this reaction is able to dissolve the carbonate according to the equation:

$$3CaCO_3 + 3H_2SO_4 = 3CaSO_4 + 3H_2O + 3CO_2. \quad (2)$$

A summary of these two equations gives:

$$2NiAS + 3CaCO_3 + 5Ag_2SO_4 = 10Ag + 2NiSO_4 + As_2O_3 + 3CaSO_4 + 3CO_2. \quad (3)$$

The direct precipitation of silver by reaction between solution and arsenides, and the dissolving of carbonate and filling up of the open space developed, are quite different things. But the dissolution of carbonate is governed by the quantity of acid set free by reaction (1). Hence, it is possible to replace both niccolite and calcite simultaneously by metallic silver. Calculating the volume changes, the increase in volume of 200 per cent, according to equation (1), will change to a decrease of 40 per cent, according to equation (3). Replacing, however, only 2 molecules of $CaCO_3$ instead of 3, theoretically there would be an increase of only 2 per cent.

It has been observed that the volume of specimens with relatively large amount of carbonate gangue was nearly unmodified, whereas specimens consisting of arsenides only, swelled and fell to pieces.

The dissolution of all elements of the hosts (Ca, Ni, Co, As, carbonic acid) and the precipitation of the guest (silver or gold) take place simultaneously. Hence, it may be inferred that these double reactions really may be termed metasomatism, provided that the volume of the total mass is not visibly changed. If, however, volume changes are taken into consideration, the question becomes more complicated and discussion of the subject would occupy too much space.

Chalcopyrite, Bornite, Covellite, Chalcocite and Cuprite.

The best results were obtained upon heating the specimens (at about 120° C.) in a concentrated solution of $Cu(OK)_2$ in KOH. Nearly equally good results were obtained with concentrated solutions of $CuSO_4$ with or without the addition of ferrous or ferric sulphates. These last replacements proceed more slowly. Many structures have already been given by Young and Moore [36] and by J. C. Ray; [37] it is thus superfluous to illustrate similar figures.

Irregular replacements of chalcopyrite along fractures and heterogeneous contacts are common, and some mutual boundaries were observed.

One of the more unusual structures is shown in Fig. 32. This resembles the well known "grating" type, *e.g.* bornite and chalcopyrite. These structures according to many observers may have several origins, such as: due to unmixing, dispersion, recrystallization or metasomatism, or due to oriented intergrowth by simultaneous deposition. In Fig. 32 it is obvious that the solutions were not exclusively guided by fractures; the chalcocite

[36] *Op. cit.*
[37] *Op. cit.*

FIG. 32. Initial stage of chalcopyrite replacement (white) by chalcocite (gray) along three crystallographic directions of chalcopyrite.

FIG. 33. Replacement of chalcopyrite (white) by bornite (gray). × 135.

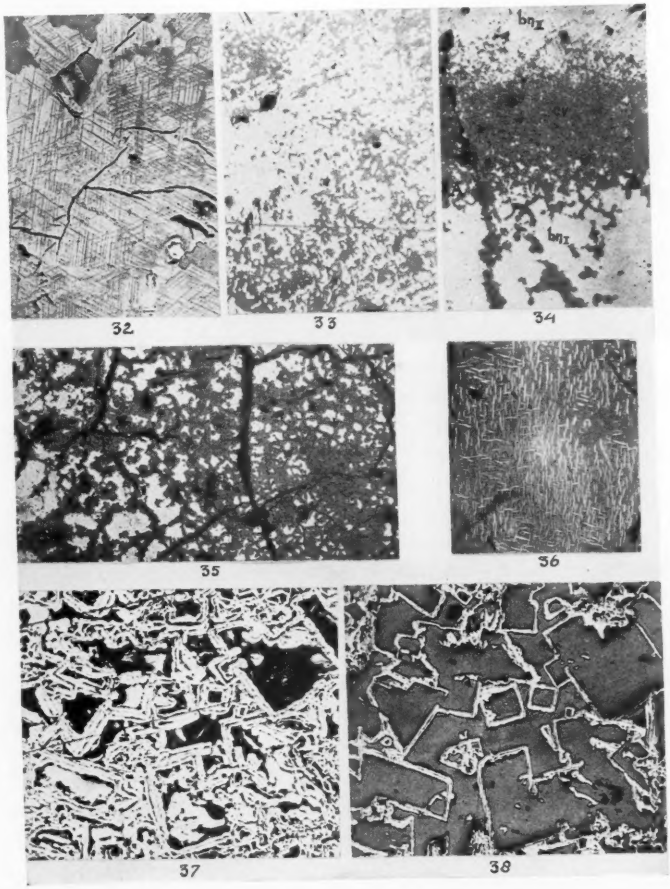
FIG. 34. Same as Fig. 4, higher magnification. Purplish brown bornite (center, bn_I) replaced by yellowish brown bornite (?) (outer rim, bn_{II}) and covellite (second rim, cv). × 34.

FIG. 35. Polished section along *AB* of Fig. 34. Replacement of bornite (white) by covellite (gray), with simultaneous development of fissures (black). × 40.

FIG. 36. Chalcopyrite inclusions (white) in bornite (gray); taken from the transition zone between original bornite and replacing covellite (not visible in field). This structure is a result of metasomatism. × 540.

FIG. 37. Complete replacement of cuprite by metallic copper (white) with loss of volume and preservation of cuprite structure. Black = pits and porosity. × 54.

FIG. 38. Same as Fig. 37. Initial stage of replacement.



FIGS. 32–38.

laths are traversed by them and are apparently older, in reality younger, than these fractures. Close inspection of this figure does not incline one to choose metasomatism as the process.

The much discussed isometric pattern of chalcocite remains open to some question. The two points of view "paramorphism of rhombic chalcocite after isometric chalcocite" a[illegible] "inherited structure"—*e.g.* from bornite or sphalerite—require further investigation. The etching patterns of synthetic chalcocite pseudomorphic after chalcopyrite sometimes resembled the so-called "lamellarer Kupferglanz" of Schneiderhöhn, although not so perfect as in natural specimens. Synthetic replacement of pyrite, however, at the same temperature of about 130°, has not yet shown the lamellar etch-pattern. It seems probable that this structure may have both modes of formation.

Replacement of chalcopyrite by chalcocite proceeds much more readily than that of pyrite. This perhaps is due to the fact, that in the former case a loss of volume results, whereas in the latter an increase in volume is involved, an idea previously suggested by Spencer.[38]

Another texture worth mentioning, approaching the so-called "graphic intergrowth," is shown in Fig. 33. This bornite was observed only in the transition zone, the ultimate stage being complete replacement by blue chalcocite.

. It is a well known fact that the reactions or replacements involved in nature by supergene enrichment of copper ores commonly proceed according to the series: pyrite-chalcopyrite-bornite-covellite-chalcocite. The reversed sequence may proceed in nature under special conditions. In synthetic replacements, complete series in both directions may be produced. Using concentrated solutions of copper, the series proceeds in the direction of copper enrichment; using concentrated solutions of ferrous and ferric sulphates, it proceeds in the reverse order, hence causing iron-enrichment. It is self-evident that in quiet solutions these reactions are balanced by the concentrations of iron and copper. In order to press the process in a certain direction the

[38] Spencer, A. C.: Econ. Geol., vol. 8, pp. 621–652, 1913.

replacing metal in solution must be present in excess. The textures obtained by the experiments are so similar to those observed in nature, that it is needless to illustrate them.

Three exceptions, however, may be noted. Fig. 34 represents at higher magnification a part of the rims shown in Fig. 4. This specim , composed of purplish brown bornite free from covellite and nearly free from chalcopyrite, was immersed in a concentrated solution of $3FeSO_4.Fe_2(SO_4)_3$ at 85° C. The "yellowish brown" compound of the outer rim (bn_{II}, Fig. 34) is probably identical with the "second bornite" described by Schneiderhöhn.[39] A polished surface along the section *AB* of Fig. 34, is shown in Fig. 35. The open fractures clearly visible in this figure did not exist in the original specimen, but are the result of the loss of volume caused by solution of the greater part of the iron. This seems strange in view of the fact that only iron solutions were used in this experiment. The shell of pure covellite might lead one to infer that the newly formed bornite (?) must be poorer in copper than the original bornite and, hence, of another composition. The solution grows richer in copper and ferrous sulphate and poorer in ferric sulphate on further penetration. But, as stated above, the reactions are balanced by the concentrations. A point may be reached where the solutions contain sufficient copper to be able to replace the purplish brown bornite by covellite, at the same time dissolving part of the iron. Between the covellite and the unaltered purplish-brown bornite, the latter gradually becomes more yellow and may yield the structure shown in Fig. 36, resembling an unmixing structure. This alteration of bornite is not owing to the increase of temperature alone, since this feature has only been observed in the transition zone mentioned above. Hence, it is not due to real unmixing. On the other hand, it is perhaps not justified to call it metasomatism without further explication.

In consequence of this apparent unmixing structure (Fig. 36) it may be emphasized that the solution of oriented inclusions upon heating a natural specimen has been recorded by several

[39] Lehrbuch der Erzmikroskopie, Bd. II, p. 344.

authors as proof of unmixing structure. This is unjustified. At the present, the possibility of unmixing or the breaking down of solid solutions in some ore minerals even at relatively low temperature will not be denied by anyone who is acquainted with the subject. At least, Fig. 36 proves that this kind of structure may be due to metasomatism at low temperature.

Another similar well-known natural phenomenon is the enrichment of silver compounds in galena remnants inclosed in cerussite, described by Emmons[40] and Spurr.[41] The experiment under discussion shows clearly that the ions of the replacing solution may indirectly bring about an unsuspected replacement; in this case, copper enrichment in certain zones with iron-solutions. After the experiment it was also plainly observed that small chalcopyrite lenses originally existing had acted as barricades to the solutions; they were not altered, whereas the covellite rims just behind them were disconnected.

It must be stated that not all bornite gave the same results if placed in a solution of $3FeSO_4.Fe_2(SO_4)_3$. Bornite from Monte Catini (Italy) and Gormanston (Tasmania) was only superficially altered to chalcocite and covellite and did not show the two rims formerly mentioned and produced in bornite from Orawitza (Hungary), Ovalle in Coquimbo (Chili), and Burra Burra (Australia).

Replacements of cuprite by metallic copper were obtained with reducing agents; a solution of $Sn(OK)_2$ in KOH being especially effective. Notwithstanding the great loss of volume by this alteration, the external structure of the cuprite grains was excellently preserved, the loss of volume being expressed by minute openings between the grains and between the zones of one grain. Fig. 37 shows complete replacement, whereas Fig. 38 shows only a moderate advanced stage. The loss of volume of this compact cuprite is well demonstrated in these figures.

Sometimes cuprite was replaced by both metallic copper and

[40] Emmons, S. F. et al.: Leadville Mining district, Colorado, U. S. Geol. Surv. Prof. Paper 148, 1927.

[41] Spurr, J. E.: Ore Deposits of Monte Cristo, Washington. U. S. Geol. Surv. Ann. Rept. 22. Pt. 2, pp. 777–865, 1901.

an unknown compound, perhaps resulting from an impurity of iron in the original homogeneous cuprite, and probably precipitated as "limonite." Now and then, colloform textures were produced which could not be observed in the original cuprite.

In addition to the replacements formerly mentioned, the following results were obtained:

(1) Chalcocite in ferrous sulphate → chalcopyrite.[42] Especially fine textures along fractures and heterogeneous contacts.

(2) Chalcocite in a solution of ferrous ammonium sulphate with excess of H_2S → bornite. In the transition zone a fine layer of chalcopyrite was observed. At heterogeneous contacts of quartz with original chalcocite two fine layers of chalcopyrite separated by a thin layer of bornite were observed.

(3) Chalcocite and covellite in a concentrated solution of ferrous sulphate, partially → bornite and chalcopyrite.

(4) Chalcocite in a solution of ferrous sulphate—perhaps slightly oxidized—with some $Na_2S_2O_3$ gave rise to the formation of a soft black coating, and beneath this coating, the chalcocite → covellite with preservation of the original rhombic chalcocite structure. Sometimes all pseudomorphic covellite grains were bordered by a thin layer of chalcopyrite, resembling an exsolution texture.

(5) Seven specimens of chalcopyrite in the same solution of $Cu(OK)_2$ → chalcocite. Specimens from Kupferberg, Müsen and Mitterberg were more resistant to replacement than those from California and Freiberg. All sections were partially replaced by chalcocite, with a thin layer of bornite in the transition zone; those of California and Freiberg especially, were also coated with fine cuprite.

(6) Covellite in a solution of $FeSO_4$ and H_2S → unknown compound with internal reflections of gray-green white color.

(7) Covellite in a solution of ferrous ammonium sulphate (without H_2S) was altered to chalcocite. Chalcopyrite, bornite and pyrite were not observed in this case.

(8) Chalcopyrite in a solution of Cu_2Cl_2 and concentrated KOH → chalcocite.

(9) Bornite and white chalcocite in a solution of $CuSO_4$ → blue mottled chalcocite, especially along fractures. Original graphic textures were preserved and could be observed after replacement by the different colors of natural and synthetic chalcocite.

(10) Chalcopyrite in $As(OK)_3$ → unknown gray compound, perhaps a copper arsenate. The chalcopyrite structure was excellently preserved.

[42] Arrow signifies "was replaced by."

(11) Chalcocite in a very dilute solution of nitric acid was coated with and → fine deep green crystals. The chalcocite beneath these crystals was altered to covellite.

(12) Covellite in $Sn(OK)_2$ → chalcocite?

(13) Covellite in a very concentrated solution of ferrous ammonium sulphate saturated with H_2S → bornite, chalcopyrite and probably pyrite.

Gypsum Replaced by Anglesite, with Remarks on Volume Changes.

A crystal of gypsum was placed for 3 days in a solution of $Pb(NO_3)_2$ at 70° C. After removing the specimen, the external form was almost completely preserved; macroscopically, the colorless and transparent crystal of gypsum had become white and subtranslucent. An outer shell of newly formed lead-sulphate, about 4 mm. thick, could easily be loosened from the unaltered kernel. A shell-like opening about ½ mm. wide was plainly visible under the binocular microscope everywhere between the newly formed anglesite and the original gypsum. The crystals of "anglesite" had assumed idiomorphic forms of needle-like or thin columnar habit towards the shell-like opening.

Here the term "replacement with some loss of volume" may be used for the moment. The dissolving of the host and the precipitation of the guest go on concurrently. In its initial stage it is a true replacement. After long continuation, however, the produced texture not only shows no evidence of replacement, but even becomes almost evidence against it.

Combined with the textures formerly discussed in the section of arsenide-replacement, where increase of volume was observed, far-reaching conclusions could be drawn. It is not the writer's intention to discuss the "law of equal volume," upheld by most investigators. In field work and in practice this "law of equal volume," or better, the supplementing statement after the definition of replacement that: "substitution commonly involves no change in volume" [43] generally holds good, especially under pressure conditions. Examining replacement textures under the microscope—*i.e.* locally and in minute details—the possibility of

[43] Bastin, E. S. et al.: *Op. cit.*, p. 586.

small increase or loss in volume should not be neglected, especially if the process takes place in open space, a fact noted also by Lindgren.[44] The loss of volume by alteration of gypsum to lead sulphate is about 48 per cent.

If a mineral grain embedded in other minerals is altered to a new mineral, with some loss of volume, the ultimate result may be a drusy cavity, affording exact evidence concerning age diversity, but wrong evidence against metasomatism.

An example still more remarkable, and proved by experimental data, is the following. A small blade of gypsum, with its two parallel faces, was clamped between two polished specimens of quartz. Next, one quarter of the sections was immersed in a solution of lead nitrate. In the two openings between gypsum and quartz at the top of the specimens, some pieces of filter paper were inserted and allowed to project several centimeters above the specimens. The gradual evaporation of the water in the filter paper brings about a slow current of solution from bottom to top, along both planes of contact between gypsum and quartz. After some days it was observed that the blade of gypsum had altered to lead sulphate; a real "hydrothermal vein structure" in miniature was produced. The small crystals of anglesite were deposited generally at about right angles to the contact planes (the "walls"), whereas in the center a series of vugs were clearly observed with the binocular microscope.

The reverse case—alteration with increase of volume in open space—may cause replacement of the walls together with simultaneous deposition of crystals in open fractures or vugs, or it may produce fragments partially replaced and concurrently crustificated. These last instances were observed by replacements of arsenides by metallic silver or gold. The crystals are "frozen" to the walls.

It is not my intention to attach too much importance to these phenomena in nature. On the other hand, one may emphasize the possibilities indicated by the interpretation of this kind of microscopic texture; they cannot be neglected. In detail, crus-

[44] Lindgren, W.: Metasomatism. Bull. Geol. Soc. of Amer., vol. 36, p. 248, 1925.

tification and "vug-filling" may be closely connected with metasomatism and may be a direct accompanying effect.

Other Replacements.

Several other replacements were also produced, the host sometimes being of unknown composition. The following may be enumerated without detailed description.

Enargite by chalcopyrite (feebly); galena by bornite (in two stages); siderite by both "limonite" and manganese oxide; siderite by metallic lead; arsenopyrite by chalcocite; arsenopyrite by cuprite; argentite by metallic silver; pyrite by cuprite (feebly); chalcopyrite by a black unknown compound, after polishing, resembled bornite (in $As(OK)_3$); proustite by both metallic silver and an unknown silver compound having a pale coffee-brown color after polishing (in water with excess of Ag_2O in suspension); covellite by an unknown compound (in a solution of $(NH_4)_3SbS_4$).

Attempts were made to produce other *replacements so as to substitute all elements of the host in one single stage.* This, of course, is much more difficult, since no chemical equation of the process can be given.

By these reactions the balance of the quantities of dissolved and precipitated material is nearly an impossibility; hence they will almost always result in increase or loss of volume. Boydell [45] has described these complicated reactions at length.

The direct synthetic replacements of this kind thus far produced have not been crowned with much success concerning the studies of textures, although replacements of carbonates by soft, porous, metal sulphides were produced beyond any doubt, commonly together with crustification. In most cases the solidity of the newly formed guest was not sufficient to permit polishing. Sometimes, under favorable conditions, governed by concentration and temperature, the metallic sulphides (guests) could be polished very well.

[45] *Op. cit.*

One of the best examples was the direct replacement of siderite by galena in a solution of $Pb(OK)_2$ and $Na_2S_2O_3$ in KOH. This replacement goes on in two stages. First, the siderite is converted probably into ferrous hydroxide, which in its turn is replaced by galena with colloform texture (as it preserves the structure of the colloform ferrous hydroxide). But the cleavage planes of the siderite sometimes are clearly visible in the colloform galena. (In a solution of PbS_2O_3 in $Na_2S_2O_3$ the galena formed is very soft and is mixed with much $PbSO_4$ and S.)

Siderite, in a solution of Ag_2SO_4, may be replaced by both metallic silver and an unknown compound, with preservation of structure. A good polish may be obtained.

Other direct replacements, such as calcite by galena, siderite by chalcocite and limonite, siderite by gold and others, gave less satisfaction; the guests generally being too soft to be polished.

DIFFERING METAL-DISPLACEMENTS IN VARIOUS MINERALS BY A ONE-SALT SOLUTION.

A single solution is capable of producing several metal-displacements from one mineral to another. In synthetic replacements this feature was observed several times on a minute scale. To prove this point, the following experiment was carried out.

Three small cubes, composed respectively of chalcocite, galena and gypsum, were mounted and fixed one upon the other. Next one side of the three cubes was polished. Opposite these polished surfaces a large polished specimen of pyrite was placed, separated from them by some sheets of filter paper. A very slow current of an $AgNO_3$ solution, moving slowly between the polished surfaces from top to bottom, was kept up for some days. After the experiment it was shown that:

1. The chalcocite was covered with metallic silver; the fissure between chalcocite and pyrite (not separated by filter paper) was filled with metallic silver.

2. The chalcocite was partly replaced by metallic silver, stromeyerite and covellite.

3. The galena, by silver and blue chalcocite.

4. The gypsum locally was feebly replaced by anglesite.

5. Sphalerite, inclosed in the pyrite specimen, in the lower part was replaced by silver, in the upper part by chalcocite.

Hence, the composition of the $AgNO_3$ solution was strongly influenced by the wall rock, and contained from top to bottom: Ag-ions, Cu-ions, Zn-ions, Pb-ions, Ca-ions.

This simple experiment demonstrates clearly that a single solution influenced by the composition of the traversed minerals may accomplish a series of replacements together with fissure-filling. Taking into account also the previously mentioned "copper enrichment" in bornite, using only solutions of ferrous and ferric sulphates, it is evident that the chemistry of even the most simple alterations may sometimes be very complicated.

In the examination of natural replacements under the microscope (in detail), neither the course taken by the solutions nor the minerals traversed are known. In a simple ore composed of quartz, carbonate, pyrite, and chalcopyrite, the supergene water with its oxidizing influence at temperatures below 100° C. may cause the formation of about 30 common minerals and about 20 rare sulphates and basic sulphates. The number of equations experimentally proved on this subject is much greater (see Schneiderhöhn [46] and R. C. Wells,[47] who both give an extended list of the literature). Although it is true that the chemistry of oxidation and cementation in the gross is known from geological reasoning, the detailed chemistry of the replacements of one definite mineral at a certain point is commonly puzzling, since most replacements in copper ores may be produced in various ways.

SUMMARY AND CONCLUSIONS.

A great many synthetic replacements in open space—especially pseudomorphic in character—were produced and examined. Various intensive replacements, up to a depth of 2 or 3 mm., suitable for macroscopic examination, may go on very rapidly under special but unusual conditions. In general, the rapidity of the

[46] Fortschr. f. Miner. und Krist., 1924.

[47] U. S. Geol. Surv. Bull. 778, 1925.

process increases in proportion as the loss of volume becomes greater. If there is increase of volume, replacement in open space may either be accelerated by the disintegration of the specimen, or retarded, if the solutions are cut off from further action, by the stopping up of the feeding channels.

Examples of volume changes in the experiments under discussion are not intended as evidence against the so-called "law of equal volume" in general but only to demonstrate their importance in detail on interpretation of microscopic textures.

The textures and structures observed are in many respects similar to natural intergrowths, as may be seen from the accompanying illustrations. This mode of investigation may be of great value for obtaining data concerning the interpretation of microscopic textures and structures with both reflected and transmitted light, especially in supergene mineralization.

The results synthetically produced may resemble natural intergrowths of the bladed, zonal, graded, lattice, mottled, colloform, graphic, exsolution, or transection type. They may closely simulate the formation of mutual boundaries, of so called "intercrystallized minerals," structures with crystallographic orientation, apparent inclusions, and vein or vug filling. Of course, pseudomorphs, veinlets, replacement veins with unsupported fragments, remnants with tongues, embayments or caries, and replacements along heterogeneous contacts, were common.

Hence, hardly one of the known textures or structures in ore specimens, considered separately, is a safe criterion against metasomatism. In addition, all primary textures and structures may be preserved. Therefore, it will frequently be nearly impossible to prove the absence of metasomatic action subsequent to the primary deposition.

Smooth contacts between minerals are not a safe criterion of simultaneity.

Traversing or cross-cutting structures commonly are confirmatory evidence of original age diversity; they do not give safe evidence as to the succession of deposition. It was shown that open, and also filled fissures, may be contemporaneous with or

even older than the traversed minerals now existing. Moreover, an apparently younger vein may be an unattackable remnant.

Drusy cavities, crustificated fragments and crustificated vein-walls of small size—especially under non-pressure conditions—may be the result of metasomatism, attended with increase or decrease of volume.

Concentric structures of different minerals are not safe evidence of simple succession in deposition or rhythmic precipitation.

Proved pseudomorphs are convincing for metasomatism; the possibility of several successive pseudomorphic replacements, however, is not excluded.

So called " interstitial fillings," do not always indicate deposition in open space, not even if the bordering minerals seem to be perfectly fresh.

The terms: " mutual boundaries," " intercrystallized minerals," " unmixing texture," and " perfectly fresh minerals," generally can not be used as safe evidence against metasomatism, unless the absence of metasomatism is secured by other observations.

The expressions: " mineral A projects into " or " cuts " mineral B, are mostly suggestive of original replacement; they do not offer conclusive proof concerning the sequence of A and B.

Replacement remnants may sometimes assume forms that seem to give positive evidence for the reverse age diversity.

Rims at heterogeneous contacts very often indicate replacement. The rims, commonly, are composed of the metasome; in places, reversely, they are remnants of the host.

If grains of one definite mineral are all broken, and the surrounding minerals do not show this feature, the probability is suggested that this broken mineral has replaced another with some loss of volume. Commonly this phenomenon is attributed to the plasticity of the matrix under pressure conditions, or, to shrinkage cracks in consequence of recrystallization from a gel.

In these experiments much evidence has been brought forward that may indicate metasomatism, although often it is not regarded as such. Reversely the foregoing points of view do not imply at all that every observed intergrowth may be interpreted as " due to metasomatism."

The solutions used in the experiments were often of such unusual and fantastic composition or concentration as to make it necessary to avoid any comparison of these synthetic replacements with natural ones as to mode of origin. Conversely, it may be said that the textures and structures produced may possibly occur in natural specimens.

For convenience, mineral names were always given to the synthetic guests, though the chemical expressions properly should have been more correct. Quantitative chemical analyses of the guests were not carried out, the metasome—determined mostly by the composition of host and solution—was affirmed microscopically.

It is unmistakable that the textures and structures produced are really due to replacement; a great advantage above natural textures, in which detail nearly always leaves some doubt as to their mode of origin.

It was shown that two or more minerals of differing chemical composition may be replaced concurrently by one new compound; moreover, all elements of the host may be substituted. Single replacements sometimes proceed in two stages, producing a " reaction rim " between host and guest.

In special cases, synthetic replacement may be a useful expedient to unravel hardly perceptible textures.

A solution containing only one salt, acting on one mineral only, on penetration may change its composition so as to cause the formation of different replacing minerals.

If a one-salt solution is allowed to act successively on several minerals, it may bring about various different replacements at the same time; a fact resembling the influence of wall rock on ore solutions in nature.

It seems probable that metacrysts by preference will develop, if both acid and basic part of the host are substituted, or if the process proceeds with some loss of volume.

A loss of volume of 20 per cent could not always be detected under the microscope. The original host structure may even be preserved by a loss of volume of about 30 per cent.

Attention was drawn to the fact that the use of diffusion cases may greatly influence the results obtained.

In these comparatively superficial investigations at issue, many problems continue unexplained; every replacement of one mineral by another may in itself be enlarged to a field of investigation if all factors concerned are considered.

Acknowledgments are due to Prof. H. F. Grondijs, in whose laboratory these experiments were carried out.

INSTITUTE OF TECHNOLOGY,
DELFT, HOLLAND.

PETROLOGY OF THE KAOLIN DEPOSITS NEAR ANNA, ILLINOIS.[1]

RALPH E. GRIM.

INTRODUCTION.

THE existence of deposits of white clays with characteristics similar to those of sedimentary kaolins located in a small area in extreme southern Illinois near Anna, Union County, has been known for some time.[2] Their valuable ceramic properties have been described,[3] and recent investigations by the Illinois State Geological Survey have shown these clays to possess high decolorizing ability.[4] As these clays are different, particularly in their mineral composition, from clays commonly used for bleaching purposes, and because they have a striking mode of occurrence, a petrologic study of them has been made.

OCCURRENCE AND LITHOLOGY.

The Anna kaolin occurs chiefly in limited bodies that range in thickness up to 110 feet and in diameter up to 300 feet. At the time the deposits were visited their margins could not be seen, but it is reported by operators of the deposits that the clay bodies are bounded on their margins by sand and lignitic substance, and that the contact between the clay and the sand in some pits is

[1] Published with the permission of the Chief, Illinois State Geological Survey. Presented before the Society of Economic Geologists, Chicago Meeting, Dec. 1933.

[2] Worthen, A. H.: Geology of Illinois, vol. III, p. 52, 1868.

[3] Purdy, R. C., and DeWolf, F. W.: Preliminary Investigation of Illinois Fire Clays. Illinois State Geol. Survey Bull. 4, pp. 173–175, 1907.

St. Clair, Stuart: Clay Deposits near Mountain Glen, Union County, Illinois. Illinois State Geol. Survey Bull. 36, pp. 71–83, 1920.

Parmelee, C. W., and Schroyer, C. R.: Further Investigations of Illinois Fire Clays. Illinois State Geol. Survey Bull. 38–D, pp. 42–64, 1921.

[4] Piersol, R. J., Lamar, J. E., and Voskuil, W. H.: Anna "Kaolin" as a New Decolorizing Agent for Edible Oils. Illinois State Geol. Survey Rept. of Inves. No. 27, 1933.

approximately vertical and that in nearly all it is marked by a zone of hard ferruginous material. Fig. 1 illustrates these phenomena and shows the general mode of occurrence of the clay. Parmelee and Schroyer [5] have emphasized also the vertical boundary of the clay.

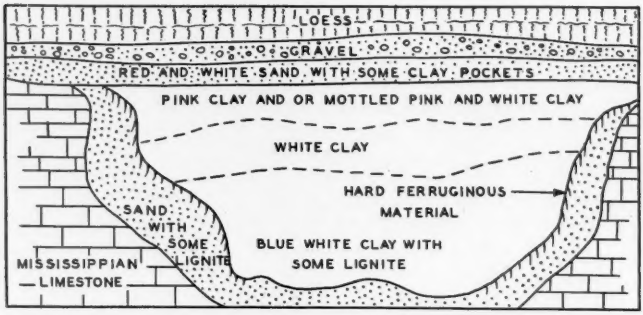

LOESS
GRAVEL
RED AND WHITE SAND WITH SOME CLAY POCKETS
PINK CLAY AND OR MOTTLED PINK AND WHITE CLAY
WHITE CLAY
HARD FERRUGINOUS MATERIAL
SAND WITH SOME LIGNITE
BLUE WHITE CLAY WITH SOME LIGNITE
MISSISSIPPIAN LIMESTONE

FIG. 1. Generalized sketch of a body of Anna kaolin, showing the relation of the clay to enclosing beds. Based on data obtained from operators.

The bedrock underlying the clay is lower Mississippian limestone, and the relations of the two suggested to St. Clair [6] that the clay bodies occupy depressions in the limestone. Actual exposures or drill records verifying this suggestion are not available, but outcrops of the limestone in the vicinity of the pits at elevations above those of the clay deposits suggest that this relationship actually exists.

The Anna kaolin is generally white or blue-white. Its upper part is commonly pigmented in streaks with red iron oxide or hydroxide, and some clay bodies are red throughout. Much of the clay is free from grit, but rare sandy lenses are encountered. The clay shows no bedding. It is plastic, has an irregular fracture, disaggregates easily, is rather brittle, and adheres strongly to the tongue. Some of the clay, particularly the bluish variety in some of the deposits, is decidedly lignitic.

[5] Parmelee, C. W., and Schroyer, C. R.: *Op. cit.*, p. 43.
[6] St. Clair, Stuart: *Op. cit.*, p. 78.

The clay is mostly immediately underlain by white or red water-bearing sand which separates it from the bedrock, and is overlain by loess, gravel, and white or red micaceous sand. The following sequence [7] of beds illustrates in a generalized way the common occurrence, starting at the bottom: (1) Sand; (2) Bluish white clay with lignitic material in basal portion; (3) White clay; (4) Pink clay and/or mottled pink and white clay; (5) Red and white sand with some clay pockets; (6) Gravel; (7) Loess.

Mineral Composition.

Samples from a number of different occurrences were studied in order to determine the mineral composition of the clay. Samples from different depths in the same deposit were studied also to determine any variations in composition with depth. In every case the mineral constituents were found to be the same. The chief constituent is kaolinite.[8] In the sandy clay, quartz grains are additional constituents, and in the red clays, ferruginous

TABLE I.

OPTICAL PROPERTIES OF KAOLINITE AND ANAUXITE FROM ANNA AND OTHER LOCALITIES.

Anna Kaolinite.	γ	$\gamma-\alpha$	Optical Character.	2V.
Kaolinite from red-streaked white clay, Ferrell prospect pit	1.568	.006		
Kaolinite from white clay near top of clay body, Goodman pit	1.567	.008		
Kaolinite from sandy white clay, Boyd prospect pit	1.567	.008		
Kaolinite from blue-white clay 15 ft. below top of clay body, Boyd pit	1.564	.008	(−)	Medium
Kaolinite from blue-white clay 23 ft. below top of clay body, Boyd pit	1.564	.008	(−)	
Other localities[a]				
Kaolinite from Hohberg, Saxony	1.569	.006	(−)	42°
Kaolinite from Sand Hill Station, So. Carolina	1.560	.007	(−)	42°
Anauxite from Bilin, Czechoslovakia	1.565	.006	(−)	36°

[a] Ross, C. S., and Kerr, P. F.: *Op. cit.*, p. 162, 1931.

[7] After Lamar, J. E., *Op. cit.*, p. 33.

[8] Ross, C. S., and Kerr, P. F.: The Kaolin Minerals. U. S. Geol. Survey Prof. Paper 165-E, 1931.

TABLE II.

DEHYDRATION OF CLAY MINERAL FROM KAOLIN, NEAR ANNA, ILLINOIS.[a]

Temp. ° C.	Moisture Loss (per cent).	Temp. ° C.	Moisture Loss (per cent).
110°	1.74	485°	11.86
160°	2.07	530°	12.28
250°	2.14	600°	12.70
300°	2.40	650°	13.19
350°	2.65	700°	13.34
375°	3.36	750°	13.41
400°	4.09	1000°	13.69
450°	11.19		

[a] Determinations made under the supervision of O. W. Rees, Illinois State Geological Survey.

TABLE III.

CHEMICAL ANALYSES OF KAOLINITE AND ANAUXITE.[a]

	1	2	3	4	5	6	7
SiO_2	43.24	52.40	44.59	53.62	50.51	46.54	54.32
Al_2O_3	37.44	31.91	36.83	29.84	31.76	39.50	29.96
Fe_2O_3	1.94	1.21	1.14	1.75	2.01		2.00
FeO	.00	.00	.00	.10	.14		
MgO	.10	.45	.39	.66	.70		.14
CaO	.94	1.24	1.02	1.23	1.40		.32
Na_2O	.12	.09	.13	.07	.27		.37
K_2O	.09	.13	.32	.35	.29		.00
TiO_2	2.50	1.21	2.17	1.23	1.40		
Ign. loss	14.06	11.98	13.63	11.60	11.90		
Total	100.43	100.62	100.22	100.45	100.38		
H_2O+	13.73	11.57	13.44	11.59	11.57	13.96	1.80
H_2O-	.27	.96	.59	1.38	1.76		.84

1. Kaolinite from red-streaked white clay. Ferrell prospect pit.
2. Kaolinite with some quartz from white clay near top of clay body, Goodman pit.
3. Kaolinite from sandy white clay, Boyd prospect pit.
4. Kaolinite with some quartz from blue-white clay 15 feet below top of clay body, Boyd pit.
5. Kaolinite with some quartz from blue-white clay 20 feet below top of clay body, Boyd pit.
6. Theoretical composition of kaolinite, $Al_2O_3.2SiO_2.2H_2O$.
7. Anauxite, Bilin, Czechoslovakia (W. F. Foshag, analyst, U. S. Geol. Surv. Prof. Paper 165-E, p. 163, 1931).

[a] Samples analysed chemically, optically, and by means of the X-ray were purified by thoroughly disintegrating the clay in distilled water, decanting the suspension, removing the clay fraction by means of porcelain filter cones, and drying it at room temperature. A microscopic examination showed that the clay mineral fraction was practically free from impurities. The chemical analyses were made under the supervision of O. W. Rees, Illinois State Geological Survey.

material is present also. A few other minerals are uniformly present in very small quantities.

Kaolinite.—The dominant and characteristic mineral is kaolinite, of the kaolinite ($Al_2O_3.2SiO_2.2H_2O$)—anauxite ($Al_2O_3.3SiO_2.2H_2O$) isomorphous series. This determination has previously been suggested by Ross [9] and by Allen [10] on the basis of optical data. Additional optical data, together with chemical analyses, dehydration curves, and X-ray data, are now available which are sufficiently similar to corresponding data for type kaolinite to confirm the identification (Tables I, II, and III, and Fig. 2).

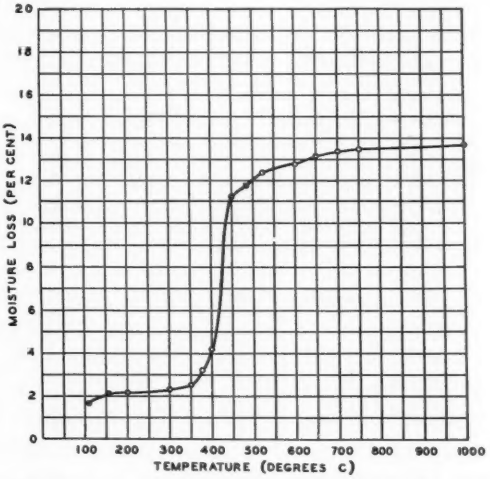


FIG. 2. Dehydration curve for clay mineral from kaolin, near Anna, Illinois.

The optical data of the clay mineral from these deposits and kaolinite from other localities agree within reasonable limits (Table I). X-ray analyses made by Professor P. F. Kerr,[11] of Columbia University, indicate the mineral to be a member of the

[9] Ross, C. S.: *Op. cit.*, p. 162.

[10] Allen, V. T.: Illinois State Geol. Survey, unpublished notes.

[11] Kerr, P. F.: Illinois State Geol. Survey, unpublished report.

kaolinite-anauxite group. The dehydration curve (Fig. 2) of the Anna clay mineral is similar to curves for typical kaolinite,[12] in showing a small moisture loss below about 375° C., a rapid loss from 375° to about 500° C., and a gradual loss from 500° to 750° C., when dehydration is essentially complete. Chemical analyses of the purified clay mineral are given in Table III. Samples 1 and 3 are very close to the theoretical composition of kaolinite. Samples 2, 4, and 5 differ essentially in showing a higher SiO_2 value. Kerr's [13] X-ray analyses of samples 1 and 3 show no line on the diffraction pattern in addition to those of kaolinite; whereas his analyses of samples 2, 4, and 5 show in addition lines characteristic of quartz. Therefore, it must be concluded that analyses 2, 4, and 5 do not indicate the presence of a kaolin mineral with a silica to alumina ratio higher than kaolinite, i.e., approaching anauxite, which has a silica to alumina ratio of about 3, but suggest rather a mixture of kaolinite and quartz. In other words, the combined chemical and X-ray data indicate that the clay mineral constituent of the Anna kaolin is kaolinite with a silica to alumina ratio approaching 2, and that where chemical analyses show a higher silica to alumina ratio, the higher silica content is to be considered as indicative of a mixture of kaolinite and quartz rather than anauxite.

The data indicate no appreciable variation in the identity or composition of the clay mineral constituent in different deposits or at different depths in the same deposit, but on the other hand show that the kaolin is composed of the single mineral, kaolinite.

In thin section, the Anna kaolinite is light grayish yellow. It occurs in particles too small for size or shape determination, but rarely, larger flake-shaped particles reaching .01 mm. in diameter are present and in a few sections larger books of kaolinite, often with a distinctly vermicular shape, can be found. These larger crystals are either scattered through the finer material or are concentrated in areas of generally more coarsely crystalline material.

[12] Ross, C. S., and Kerr, P. F.: *Op. cit.*, p. 166.
[13] Idem.

Quartz.—Quartz in unsorted grains is a rare constituent in the non-sandy clay, and an abundant to dominant constituent in the sandy variety. The grains range in size from colloidal, in which case their presence is indicated by X-ray analyses, up to 0.2 mm. The larger grains are usually well rounded. Their extinction shows them to be unstained. They show no evidence of any secondary addition or removal of silica.

Ferruginous material.—Ferruginous material in the form of iron oxide or hydroxide occurs as a pigment disseminated through the red clays. The individual particles are mostly too small to be detected microscopically. Rarely the ferruginous material is concentrated around openings in the clay as if the openings originally contained the source material of the iron, but in no instance could definite evidence be obtained that this was the case.

Other minerals.—Kyanite, zircon, staurolite, tourmaline, ilmenite, leucoxene, rutile, sillimanite, epidote, anatase, chloritic material, feldspar, and pyrite occur in about this order of abundance as rare constituents of the kaolin. They occur in grains as much as 0.2 mm. in maximum diameter and are commonly rounded. Except for the ilmenite, which commonly is changed to leucoxene, these minerals exhibit little or no alteration.

A noteworthy feature of the Anna clays is the rarity of feldspar. A very few grains of microcline and orthoclase were found in only one sample studied. Pyrite occurs chiefly in the blue-white clay as a rare constituent in the form of irregular aggregates of well crystallized grains which are probably authigenic.

Texture.

With the possible exception of the pigmentary iron oxide or hydroxide, all the material composing the Anna kaolin is crystalline. The rock is essentially composed of particles of kaolinite too small for size or shape determination even under high magnification. In some samples, the individual particles exhibit no uniformity of orientation; this, with their small size and the low birefringence of the mineral, produces an almost isotropic appearance. Mostly, however, local irregular places in the rock

have a fairly uniform orientation. These are surrounded by clay in which the orientation is less uniform, or in which the crystallographic direction of the particles in the aggregate varies so that when a thin section of the kaolin is rotated between crossed nicols a hazy cloud-like distribution of clay masses results. The other minerals are scattered through the kaolinite.

ORIGIN.

According to St. Clair, "the clay deposits . . . are thought to have been deposited in an arm of the Tertiary Gulf embayment . . . the clay having been deposited in depressions which existed in the old land surface."[14] At the present time the deposits are not opened sufficiently to permit definite conclusions regarding their origin. However, the present study has produced evidence for certain features of genesis, some of which are in agreement with St. Clair's interpretations.

The "heavy" minerals of the Anna kaolin are different from those of the nearby Pennsylvanian beds[15] in their content of kyanite, staurolite, and sillimanite, and their deficiency in garnet. They differ similarly from the Chester sandstones[16] of southwestern Indiana, the mineral composition of which is probably the same as that of equivalent Mississippian beds in Illinois. The "heavy" minerals of the Anna kaolin are identical with those of the lower Tertiary[17] and possibly those of the late upper Cretaceous formations of the Mississippi embayment.

The "heavy" minerals, therefore, provide strong evidence that these clays are of late upper Cretaceous or lower Tertiary age, at which time the Mississippi embayment is known to have ex-

[14] St. Clair, Stuart: *Op. cit.*, p. 79.

[15] MacVeigh, E. L.: Mineralogic Studies of Some Pennsylvanian Sandstones. Unpublished thesis, University of Illinois, 1932.

[16] McCartney, G. C.: A Petrographic Study of the Chester Sandstones of Indiana. Jour. Sed. Petrol., vol. 1, pp. 82–90, 1931.

[17] Grim, R. E.: The Eocene Sediments of Mississippi. Unpublished thesis, State University of Iowa, 1931. The Petrography of the Fuller's Earth Deposits, Olmstead, Illinois. Econ. Geol., vol. 28, pp. 344–363, 1933.

Lamar, J. E., and Sutton, A. H.: Cretaceous and Tertiary Sediments of Kentucky, Illinois, and Missouri. Amer. Assoc. Petr. Geol., vol. 14, p. 863, 1930.

tended into southern Illinois. They indicate also that the sand mineral grains of the clay bodies have not been derived locally from adjacent Mississippian and Pennsylvanian beds, but have had the same source as sediments of the same age in the embayment area. The ultimate source [18] of these sediments in the eastern part of the embayment is believed to be in the Appalachian area. It is possible that this distant source-area supplied the clayey as well as the sandy components of the clay bodies, but it is possible, on the other hand, that the adjacent area of Mississippian and Pennsylvanian rocks supplied much of the finer clayey material, whereas the coarser grains came from the distant source-area.

These considerations favor the interpretation that the Anna clays were deposited in an arm of the late upper Cretaceous or lower Tertiary embayment, or in the flat coastal area bordering such an arm of the embayment. The surrounding area must have been low, flat, and possibly humid, so that it yielded no sand debris to the area of accumulation, since all the sand probably came from the same area as the heavy mineral grains. Whether the adjacent area yielded the fine clayey fraction of the kaolins, the coarser debris being brought in by currents from the embayment to the south and ultimately from a more distant source, or whether the adjacent area supplied little or no detrital material, the coarse and fine alike coming from the distant source area, cannot be determined. It seems probable, however, that the adjacent area supplied at least a portion of the finest debris.

An alternative explanation is that the Anna kaolin deposits are of later Tertiary age and had their source in early Tertiary or late upper Cretaceous sediments of the embayment area. There is no evidence for this alternative, but neither can it be disproved.

In the description of the occurrence of the Anna kaolin, it has been noted that the contact between the clay and surrounding sand or lignitic material is commonly sharp and almost vertical. It is evident that such relations are not depositional, but must have resulted from post-depositional changes in the clay and enclosing material. Similar characteristics are shown by the

[18] Grim, R. E.: The Eocene Sediments of Mississippi. Unpublished thesis, State University of Iowa, 1931.

flint and diaspore clays of Missouri, which McQueen [19] explained as the result of the formation of sink holes in the limestone beneath the clay, and the slumping of the clay into these depressions. No other sequence of events appears adequate to account for the relation of the clay to the enclosing material, and the general shape of the Anna clay bodies. Their characteristics suggest that the slumping or collapse took place after the deposition and consolidation of the clay. It is entirely possible that the Anna kaolin was originally a more or less continuous blanket deposit, and that sink hole action, followed by slumping and collapse of the clay into the solution cavities in the underlying limestone, served to protect it from the later erosion which removed the clay from the intervening areas.

The constancy in the composition of the clay mineral and the absence of any evidence for secondary movement of silica in the various deposits near Anna and at different depths in the same deposit suggest that there has been no appreciable postdepositional alteration of the clay.

RELATION OF BLEACHING ABILITY OF CLAYS TO THEIR PETROGRAPHIC CHARACTERISTICS.

It has been shown previously [20] that the bleaching clays generally used in this country are entirely crystalline and are composed essentially of montmorillonite, and that their bleaching ability is unrelated to texture. Domestic kaolinite clays have not been used for bleaching purposes. They have been considered to have no natural bleaching action [21] and to be unsuited for activation. It has been known that they possess decolorizing ability after ignition. However, at least some English china clay [22] has been known for some time to possess bleaching ability

[19] McQueen, H. S.: Geologic Relations of the Diaspore and Flint Fire Clays of Missouri. Jour. Amer. Cer. Soc., vol. 12, pp. 687–697, 1929.

[20] Grim, R. E.: Petrography of the Fuller's Earth Deposits, Olmstead, Illinois. Econ. Geol., vol. 28, pp. 344–363, 1933.

[21] Nutting, P. G.: The Bleaching Clays. U. S. Geol. Survey, Circ. 3, p. 4, 1933.

[22] Anon.: China Clay and Petroleum. Chem. Age (China Clay Trade Review Section), vol. 10 (248), p. 9, 1924.

before ignition. It has recently been shown that Anna kaolin [23] has high decolorizing ability and that most American kaolins do not have this property.

The decolorizing ability of bleaching clays when inherent or produced by activation appears to be related to properties of the clay mineral particles [24] that constitute the greater part of the clay. The discovery of bleaching kaolins indicates that the ability to bleach is not limited to montmorillonite, but is occasionally possessed by kaolinite, and it is entirely probable that other clay minerals besides montmorillonite and kaolinite may also possess decolorizing properties.

An analysis of the properties of the clay minerals known to possess bleaching ability should throw light on the cause of bleaching action. Although little information bearing on the properties of these minerals is available, sufficient knowledge is at hand to show what might be expected from such investigations. Montmorillonite is known to have high base-exchange capacity,[25] whereas in kaolinite the capacity is small. Thus, decolorizing ability appears to be unrelated to base-exchange capacity. Montmorillonite and kaolinite have very different dehydration characteristics. Montmorillonite loses a large part of its water at low temperature (200° C.) whereas kaolinite loses very little water below 400° C. Therefore, decolorizing ability is not necessarily related to loss of moisture at low temperatures.

According to Nutting,[26] bleaching ability is due to the existence of open bonds, mostly on the surface, but rarely in the interior of a grain. They may exist naturally or be developed by activation. Commonly, associated water is removed to leave open bonds, but the removal of almost any element or group, or simply an interchange, may produce it. Activated surfaces are not limited to clay minerals, but may be developed in many minerals by suitable

[23] Piersol, R. J., Lamar, J. E., and Voskuil, W. H.: *Op. cit.*

[24] Grim, R. E.: *Op. cit.*, ECON. GEOL., vol. 28, p. 361.

[25] Mattson, Sante: Laws of Soil Colloids III, Isoelectric Precipitates. Soil Sci., vol. 30, pp. 459–494, 1930. Kelley, W. P., Dore, W. H., and Brown, S. M.: The Nature of the Base-exchange Material of Bentonites, Soils, and Zeolites. Soil Sci., vol. 31, p. 43, 1931.

[26] Nutting, P. G.: *Op. cit.*

means. This concept seems to be the most satisfactory explanation of the bleaching ability of clays yet suggested and it accounts fairly successfully for the bleaching ability or the possibility of activation of some other minerals.

Fogle and Olin [27] have recently attempted to show, on the basis of the chemical characteristics of the calcium content of fuller's earth, that zeolites are important constituents of fuller's earths. This is contrary to mineralogic data, for in none of the bleaching clays studied has there been any evidence of the presence of zeolites. The X-ray diffraction patterns [28] of montmorillonite bleaching clays afford particularly strong evidence for the absence of zeolites in that the finer-grade sizes of these earths show no lines other than those of type montmorillonite. However, it must not be concluded from this observation that zeolites do not have decolorizing ability, but it can be concluded that zeolites do not occur in the fuller's earths studied.

ILLINOIS STATE GEOLOGICAL SURVEY,
URBANA, ILLINOIS.

[27] Fogle, M. E., and Olin, H. L.: Clarifying Action of Fuller's Earth. Ind. and Eng. Chem., vol. 25, pp. 1069–1073, 1933.

[28] Grim, R. E.: *Op. cit.*, ECON. GEOL., vol. 28, p. 361.

ADDITIONAL LIMONITE TYPES OF GALENA AND SPHALERITE DERIVATION.

ROLAND BLANCHARD AND P. F. BOSWELL.

At the time our first paper on "Oxidation Products Derived from Sphalerite and Galena" was written (1927), observations had been confined to occurrences in Western North America. Since that time they have been extended to other portions of the earth, more recently to Australasia, a region characterized by many oxidized ore bodies.

Observations recorded in the original paper have stood the test of time, and the two key structures for lead minerals therein defined, namely "cleavage" boxwork and "partially sintered" limonite crusts, have been confirmed as the principal identifiers of lead minerals in leached outcrops and gossans. The same holds true for the cellular boxworks and the limonite sponge derived from sphalerite.

Field observations during the last few years have disclosed, however, distinctive limonite types for both galena and sphalerite other than those previously discussed, and have established as standard certain structures which at the time the first paper was written were regarded as probably local. The purpose of this paper is to describe these more recently established standard structures.

Technical terms are used in the same sense as in previously published papers, with which the reader is presumed to be familiar.[1]

[1] White, Charles Henry: Prospecting for Disseminated Copper by a Study of Leached Croppings. Eng. & Min. Jour., Mar. 22, 1924.

Morse, H. W. and Locke, Augustus: Recent Progress with Leached Ore Capping. Econ. Geol., vol. 19, no. 3, April–May, 1924.

Blanchard, Roland and Boswell, P. F.: Notes on the Oxidation Products Derived from Chalcopyrite. Econ. Geol., vol. 20, no. 7, Nov., 1925.

Locke, Augustus: Leached Outcrops as Guides to Copper Ore. Williams &

OXIDIZED LEAD PRODUCTS.

Limonite of Galena Derivation.

"Cleavage" Boxwork.—"Cleavage" boxwork as described in the original paper, with its strongly defined cubical pattern, remains the outstanding "key" structure that identifies limonite derived from galena. Commonly it is merged with, and to a large extent obscured by, other limonite types, because before limonite derivatives appear, galena ordinarily passes through both the sulphate and carbonate stages, which yield a different limonitic product. But to some extent "cleavage" boxwork is present in nearly all limonite of lead derivation except possibly the relief type, described below.

"Partially sintered" limonite crusts (Fig. 1) are in large part pseudomorphic replacements by limonite of the cerussite that formed subsequent to deposition of limonitic jasper along the cleavage planes. They possess lower silica content than does the

---

Wilkins, Baltimore, Md., 1926.

Boswell, P. F. and Blanchard, Roland: Oxidation Products Derived from Sphalerite and Galena. ECON. GEOL., vol. 22, no. 5, Aug., 1927.

Wisser, Edward: Oxidation Subsidence at Bisbee, Arizona. ECON. GEOL., vol. 22, no. 8, Dec., 1927.

Blanchard, Roland and Boswell, P. F.: Status of Leached Outcrops Investigation. Eng. & Min. Jour., Feb. 18 and Mar. 3, 1928.

Trischka, Carl, Rove, Olaf N. and Barringer, D. Moreau: Boxwork Siderite. ECON. GEOL., vol. 24, no. 7, Nov., 1929.

Boswell, P. F. and Blanchard, Roland: Cellular Structure in Limonite. ECON. GEOL., vol. 24, no. 8, Dec., 1929.

Anderson, A. L.: The Incipient Oxidation of Galena. ECON. GEOL., vol. 25, no. 5, Aug., 1930.

Blanchard, Roland and Boswell, P. F.: Limonite Products Derived from Bornite and Tetrahedrite. ECON. GEOL., vol. 25, no. 6, Sept.–Oct., 1930.

Anderson, A. L.: Notes on the Oxidation of Jamesonite, Sphalerite and Tetrahedrite. ECON. GEOL., vol. 27, no. 8, Dec., 1932.

Also the following related, more strictly technical papers:

Posnjak, E. and Merwin, H. E.: The Hydrated Ferric Oxides. Amer. Jour. Sci., 47, p. 311, 1919. The System Fe_2O_3–SO_3–H_2O. Jour. Amer. Chem. Soc., 44, p. 1965, 1922.

Posnjak, E. and Tunell, George: The System CuO–SO_3–H_2O. Amer. Jour. Sci., 18, p. 1, 1929.

Tunell, George and Posnjak, E.: The Stability Relations of Goethite and Hematite. ECON. GEOL., vol. 26, pp. 337–343, 1931. A Portion of the System Fe_2O_3–CuO–SO_3–H_2O. Jour. Phys. Chem., 35, p. 939, 1931.

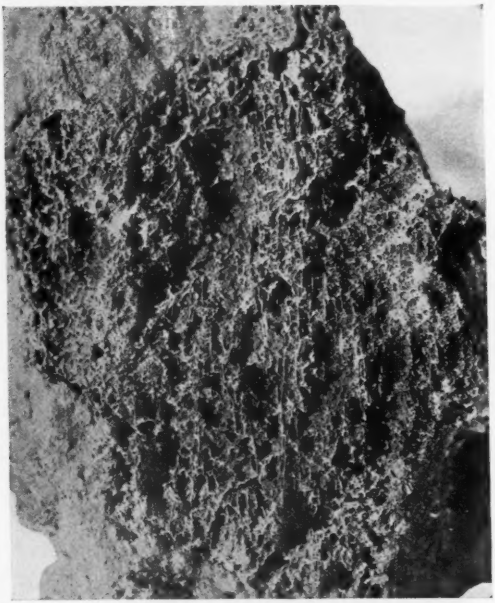


FIG. 1. "Cleavage" boxwork, loosely coated with masses of "partially sintered" limonite crusts. Note thinness and rigid parallelism of boxwork walls. "Cleavage boxes" are patterned after the cubic cleavage of galena. They are composed of limonitic jasper, whose iron and silica were imported by ground waters during incipient oxidation, and which "ate" their way into the massive galena by penetrating along cleavage planes. Ordinarily the boxwork is less well preserved than in this specimen. Lawn Hill, Queensland. × 1½.

cellular structure. Since most galena passes through the sulphate and carbonate stages before going to limonite, it is readily understandable why in the average leached outcrop of lead derivation, partially sintered crusts constitute from 50 to 90 per cent of the lead-derived limonite products.

Diamond Mesh Boxwork.—A common variation from "cleavage" boxwork—one which at the time the first paper was written was regarded as a local type—is diamond-mesh structure.

In this structure, the rigid parallelism of "cleavage" boxwork gives way to an imperfectly formed, unsymmetrically connected diamond mesh, suggestive of a rope hammock that lies rumpled upon the ground instead of being stretched to emphasize the diamond pattern. More or less parallelism of the major ribs occurs, and occasional minute cubic "boxes" are present also, but they do not constitute the predominating structure.

Next to the diamond-mesh pattern itself, the outstanding feature in this boxwork is the fact that the major ribs, which in the hand specimen have an apparent thickness of 0.2 mm. to 0.5 mm., are composed of two or more closely spaced, rigidly parallel, minutely thin webs, each similar to the single-walled major rib of "cleavage" boxwork, rather than being a solid rib of limonitic jasper as is the case with other boxworks. This double-walled structure, though not readily detectable by the unaided eye, is plainly visible under the hand lens. It has not been satisfactorily photographed, but the distinguishing features are sketched in Fig. 2, *B*.

As with "cleavage" boxwork, cell walls of the diamond-mesh product are commonly coated with partially sintered limonite crusts, but in most instances the mesh stands out emphatically despite such coating.

Of the various limonite types heretofore described, diamond-mesh structure probably resembles most closely the triangular boxwork derived from bornite. The two types may be distinguished as follows:

1. In the bornite product the structure, though triangular, is not closely meshed; in shape it resembles discordantly scattered spherical triangles rather than a dominant interlacing diamond-mesh pattern.[2]

2. Major ribs of the bornite product are single walled and solid; those of the lead product are double walled, composed of very thin parallel webs with empty space between.

3. Partially sintered limonite crusts of bornite derivation, when coating or filling the cellular structure, are composed of particles

[2] See Fig. 1, p. 559, and Fig. 2, p. 560, ECON. GEOL., vol. 25, 1930.

closely aggregated, like mud dabs in a swallow's nest, and with the crusts occupying most of the cellular volume; corresponding crusts of lead derivation are more loosely aggregated, and rarely occupy more than 25 to 40 per cent of the cell volume.

4. "Velvety" relief [3] is characteristic of the bornite product, in the hand specimen. A more dull-surfaced relief, or "dead burn," characterizes the lead product.

FIG. 2. *A*. "Cleavage" boxwork, derived from galena of the orthodox, cubic cleavage type, as it appears when divested of the partially sintered limonite crusts. The long, minutely thin, parallel ribs, and the cubic "boxes," are replicas of galena's cubic cleavage. They prove that the limonitic jasper of which they are composed penetrated along the galena's cleavage planes during incipient oxidation, before the sulphide residuals had been converted into anglesite and cerussite from which the partially sintered crusts of Fig. 1 were derived. Lawn Hill, Queensland. × 3.

B. Diamond-mesh boxwork, derived from "steel" galena. Note the irregular diamond-mesh structure, with only rare "cubic boxes." Note particularly the pairs of closely spaced, rigidly parallel, minutely thin webs that constitute the structure's major ribs. The empty space between these pairs of thin parallel webs (see arrows) has not been to date satisfactorily accounted for. Commonly the boxwork is coated with crusts of the partially sintered limonite, which in part obscure the diamond-mesh pattern. Ruby Hill, Eureka, Nevada. × 3.

Pyramidal Boxwork.—Identified with both "cleavage" and diamond-mesh structures, but much less common in occurrence, is pyramidal boxwork. Figs. 3, 5 and 6 illustrate the structure. This product is patterned after the cubic cleavage of galena, but with retreating structure, giving rise to a step-pyramid effect. It has been observed only in outcrops exposed to weathering and

[3] For description of "velvety" relief see *Idem*, p. 568.

partial erosion under sheltered conditions,—not, to date, in exposures underground.

Limonite plates in this boxwork are rigidly parallel, but with shrinkage spaces between. The plates are more or less coated

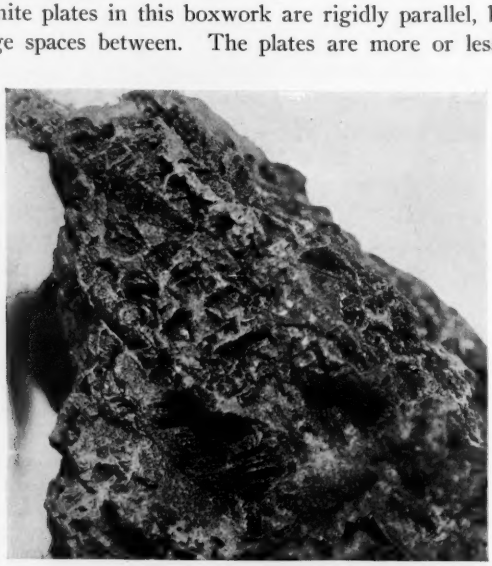


FIG. 3. Pyramidal boxwork, preserved within a matrix of intermixed relief limonite and gangue. Note, particularly in the upper left, the step-pyramid effect. Parallel shrinkage spaces develop in pyramidal boxwork, as if the structure were composed of thick mica plates with alternate plates removed. Partially sintered limonite crusts bind the plates firmly together and maintain the structure's rigidity. Pyramidal boxwork has been observed only in surface outcrops, under partial or complete shelter from weathering attacks. Aravaipa, Arizona. × 1½.

with the partially sintered limonite crusts, which bind plates firmly together, and preserve rigidity for the structure.

The reasons for development of systematic open spaces between plates, as though the structure were composed of thick mica plates with alternate plates removed, are not understood, but the condition is common, particularly in limestone, but also in various other gangues. The boxwork has been observed at Tintic (Utah),

Eureka (Nevada), Aravaipa (Arizona), the San Javier region (Sonora), Broken Hill (New South Wales), Lawn Hill (Queensland), and in numerous other lead districts.

Pyramidal boxwork has not been observed as characteristic of limonite derived from other sulphides. Though much less abundant than " cleavage " and diamond-mesh structures, it stands out as a distinguishing and unmistakable galena type.

Cellular Sponge.—The three boxworks above described occur in deposits from which well crystallized galena has been leached. All preserve to a greater or less degree the cubic structure of galena, though in the diamond-mesh boxwork that structure is subordinate.

When the galena pattern in the sulphide specimen is semi-granular to granular in form, as is commonly the case where primary lead mineralization has taken place along shale, sandstone, or quartzite bedding planes, or has partly or wholly replaced medium to fine-grained schist or sedimentary beds other than limestone, a cellular sponge normally constitutes the leached product. In pattern this does not differ essentially from cellular sponge derived from sphalerite, but the texture is finer, with cell diameter ordinarily averaging not more than 0.075 mm. to 0.5 mm.

Strong magnification ($\times$ 20 to 30) shows that in many instances this semi-granular to granular pattern for galena, in the sulphide specimen, comprises imperfectly formed aggregates of minute, interlocking cubic crystals. The leached product, under high magnification, likewise shows the sponge product to be composed in part of similarly minute, interlocking cubic " boxes " of limonitic jasper, but ordinarily so imperfectly knit together that the pattern gives the impression of being a sponge-like cluster of small limonitic cells.

Cell walls of the sponge are in all cases extremely thin and fragile, of characteristic 0.005 mm. to 0.05 mm. galena-derived thickness. In some districts, as at Eureka and Ely (Nevada), cell walls may be mostly uncoated, with semi-vitreous luster. In other districts, as at Park City (Utah), Broken Hill (New South Wales), Mount Isa and Lawn Hill (Queensland), cell walls may

be to a large extent obscured by coatings of the partially sintered limonite crusts of cerussite derivation, and the leached product in such cases does not differ greatly from ordinary partially sintered limonite crust masses, except that a sponge-like aggregation of minute, thin-walled cells emerges indefinitely through the crusted mass. In no place thus far observed does cellular sponge constitute more than 10 per cent. of the leached outcrop over an area of, say, 100 square feet.

Galena-derived sponge has not been successfully photographed. The following features differentiate it from the corresponding sphalerite product:

1. Characteristically finer cells, with more even cell structure of the galena product, averaging 0.075 mm. to 0.5 mm. in diameter, as against 0.2 mm. to 2.0 mm. for the sphalerite product. (This is not invariable, and by itself is not conclusive.)

2. Cell walls, when uncoated, have comparatively smooth surfaces, with a semi-vitreous luster; and when coated, carry the partially sintered limonite crusts of cerussite derivation; as against the crinkled, angular cell wall of sphalerite derivation, with its dull, shriveled appearance, and its scattered limonite grains, rosettes, and crinkly projections characteristic of all limonite products derived from sphalerite.

Limonite of Cerussite and Anglesite Derivation.

Partially Sintered Limonite Crusts.—Partially sintered limonite crusts, as pointed out in the previous paper, are not derived directly from galena. They represent pseudomorphic replacement of cerussite, and more rarely anglesite. Since galena normally passes through the sulphate and carbonate stages before going to limonite, it is not surprising that most cellular boxwork derived from galena is coated with these crusts, as shown in Fig. 1, and that such crusts constitute the predominating "key" structure for identification of any leached outcrops derived from lead minerals. Except where relief limonite, discussed below, is present, the limonitic crusts ordinarily constitute from 50 to 90 per cent. of

FIG. 4. Cellular sponge derived from sphalerite. Note irregular cell structure, and nearly empty cells with thinly scattered limonite grains on cell-wall surfaces. Empire Zinc Mine, Hanover, New Mexico. × 1½. (Reproduced from ECONOMIC GEOLOGY, vol. 22, page 429, 1927.)

Cellular sponge derived from galena has not been successfully photographed. The cellular pattern is similarly irregular but of much finer texture. Cell walls are usually so thoroughly coated with the partially sintered limonite crusts of cerussite derivation that the cellular sponge emerges only faintly from the mass.

the total limonite yielded in an outcrop by all leached lead minerals combined.

As described in the original paper, these crusts have a partially sintered appearance, like the surface of dead-burned magnesite brick but slightly rougher. Crusts are from two to ten times as thick as cell walls of the boxwork, and often extend out into the cell sufficiently to reduce cell diameter by one half. Generally they are loosely aggregated, and occur more or less in clusters, which subsequently may become "sintered" by weathering processes.

Relief Limonite.—Relief limonite is so called because the product comprises a pulverulent mass consisting of fluffy, loosely adhering particles that resemble powdered sugar sprinkled over a surface. The fluffy texture imparts to the product distinct relief, as contrasted with the characteristically dull and earthy, or flat and "dead" appearance of certain other limonites of the non-cellular type.

The product is not necessarily of sulphide origin. It forms wherever iron-yielding minerals oxidize in an environment of strong gangue neutralizer, such as limestone, or where strong neutralizer is introduced by ground waters into an oxidizing iron-yielding mass. The iron may have been derived from disintegrating magnetite, garnet, epidote or chlorite, as well as from various sulphide minerals. Likewise, it may have been imported by iron-bearing ground waters from a distance, and from an indefinite source.

Because of its many possible sources of derivation, relief limonite is difficult to classify as to origin. When of sulphide origin it commonly shows through the pulverulent mass minute projections of limonite rosettes, or indefinite cellular structures that stand out under the hand lens like objects in a stereoscopic slide. These cellular patterns are broken replicas of "key" structures for chalcocite, bornite, or other original sulphide mineral. Since they are seldom present in relief limonite of non-sulphide origin, their presence aids greatly in identification of the product which contains them, and unless some one of the "key"

structures is recognizable within the mass, determination of the origin of a given relief limonite is usually impossible.

Such limonite derived from lead minerals is more dull and earthy, and possesses a lesser volume of "key" structures, than

5

6

FIG. 5. Pyramidal boxwork, partly preserved within a matrix of cellular sponge and relief limonite of mixed galena-sphalerite derivation. Presumably the "step pyramids" were originally as distinct and coherent as those of Fig. 3, but nearly fifty years exposure to rain and sandstorms has corraded their outer surfaces. Block 14, Broken Hill, New South Wales. × 1¼.

FIG. 6. Pyramidal boxwork, preserved within a matrix of partially sintered limonite crusts. Erosion has removed most of the pyramid apexes, but the "mica plate" structure is well preserved. Occasional "ghosts" of "cleavage" boxwork emerge from the matrix, testifying to the product having been derived from essentially pure galena and cerussite. Unnamed prospect near Tepic, Nayarit, Mexico. × 1¼.

do relief limonites derived from most other sulphides. This makes the product particularly difficult to identify. When derived (through anglesite) from fine-grained, non-massive galena that has oxidized in a limestone gangue, it is difficult to distinguish

from limonite derived through oxidation of fine-grained, semi-massive or finely disseminated pyrite in the same gangue. Instances have been noted where the product could not be differentiated under the hand lens from relief limonite of epidote or chlorite origin. Usually, however, under a 20 × or 30 × hand lens the lead product is found to contain finely and indefinitely formed cellular structures, with coatings of partially sintered limonite crusts, emerging faintly from the pulverulent mass. Occasionally one or more of the galena boxwork remnants may likewise be clearly distinguished.

Of the various sulphide-derived relief limonites, the lead product remains the most difficult to identify, and years of field experience have not brought us to the point where we can classify it with assurance unless we find it grading into one of the lead minerals, or into one of the more distinctive lead-limonite types; or unless the gangue is free from epidote, chlorite, or other minerals whose oxidation products it closely resembles.

Relief limonite is the most common direct ferric derivative from anglesite. It is a direct derivative also from cerussite, but not in nearly as great amount as are the partially sintered crusts. Because of this fact, and the fact that anglesite ordinarily passes through the carbonate stage before yielding its ferric equivalents, relief limonite of lead origin, in the interpretation of leached outcrops, is quantitatively much less baffling than it is in a qualitative sense.

OXIDIZED ZINC PRODUCTS.

Limonite of Sphalerite Derivation.

Cellular Boxwork and Cellular Sponge, characteristic of limonite derived from sphalerite and its oxidized equivalents, were described in the previous paper. Distinguishing features of zinc-derived limonites, aside from their cellular patterns, are the dull and shriveled angular cell walls, coated with scattered limonite grains, rosettes, and small, crinkly limonitic projections (Fig. 4).

These cellular boxworks and sponges have been confirmed as the characteristic and predominating limonite products derived

from zinc minerals. Only one distinctive additional type has been identified. This, though well distributed about the world, is missing in many important districts, and where present occurs in relatively small amount.

Limonite Moss.—The additional zinc-derived limonite in the hand specimen resembles long, loosely interconnected flakes and shreds of limonite that fill and overrun the cellular structures, much as Spanish moss overruns and locally masks the limbs and foliage of trees. Its resemblance in pattern to Spanish moss is so close that the term limonite moss has been applied to the product.

Though the limonitic shreds anastomose to some extent, their long dimensions are mostly parallel, and under the hand lens the product's structure suggests a stalactitic origin. The fact that the moss, when found in place, invariably points steeply downward, lends strong support to the stalactitic origin.

Slender stalactitic deposition of limonite commonly accompanies pyrite oxidation, also, and has been found at one place (Duquesne. Arizona) to accompany oxidation of chalcocite with which a preponderant amount of pyrite is associated. It has not as yet been found to be characteristic of oxidation products derived from single sulphides other than sphalerite and pyrite.

The sphalerite and pyrite products may be differentiated from each other as follows:

1. Individual shreds of sphalerite moss are generally slender, rarely exceeding 0.5 mm. in diameter. They possess in miniature the characteristic dull, shriveled appearance of dried ragweed stalks. The shreds themselves have been found only deposited upon or adjacent to cellular boxwork or sponge derived from sphalerite, and their shriveled surfaces commonly carry the same minute limonitic projections that characterize cell-wall coatings of other sphalerite products. Superficially, a small mass of the product does not differ greatly in appearance from a similar mass of shredded wheat biscuit, except for its more slender shreds and its usual brown to brownish-black color.

2. The stalactitic equivalent of pyrite derivation commonly

involves a coarser structure, comprising irregularly fluted limonitic jasper columns of 1 to 10 times greater diameter than the sphalerite-moss shreds. Where only the mossy shreds exist in the pyrite product, as contrasted with the customary fluted columns, the shreds invariably are coated with the smeary crusts, or with the minute nodular limonite pinpoint (miniature botryoidal) crusts described in previous papers as characteristic of pyrite-derived limonite. Such crusts are dark brown to black or iridescent in color, and have a submetallic luster instead of the dry and shriveled appearance of sphalerite-derived moss.

Once the two limonite-moss types have been accurately distinguished in the hand specimen, they are not likely to become confused.

Limonite moss of sphalerite derivation does not ordinarily occur in masses of more than 2 cm. to 3 cm. length, and has not thus far been found deposited more than a few centimeters from the point of probable origin.

Limonite of Smithsonite Derivation.—In contrast to cerussite, pure smithsonite has not been found to yield distinctive limonite products except in minute amount.

In certain districts, characteristic limonitic derivatives grade into smithsonite in a manner that leaves no doubt as to their origin. They ordinarily consist of small, indefinitely formed and loosely adhering aggregates of the limonite grains, rosettes, and irregular fine angular projections, already described, as coatings of cell walls in the sphalerite-derived cellular structures. But they are so fragile that, unless supported by cellular structures, they rarely persevere through the shock of a light blow of the pick imparted to the limonitic mass of which they are composed.

Usually such limonitic aggregates grade insensibly within 1 mm. to 2 mm. into limonite products of pyrite derivation, or into products of wholly undetermined origin such as the undifferentiated relief types. In such cases they cannot well preserve an independent identity, and persistent search over many portions of the earth for a dependable " key " limonite product of exclusive

smithsonite derivation has been disappointing. As a consequence, we have been successful in estimating quantitatively the former zinc content of a leached outcrop only in districts containing substantial amounts of the sphalerite-derived cellular structures.

Fortunately, in most zinc districts such cellular structures are importantly preserved. But, under the most favorable conditions, estimation of former zinc content in a leached outcrop is more difficult and uncertain than estimation of former lead content.

Possibly the fact that pure smithsonite is less coherent than cerussite, plus the greater solubility of $ZnCO_3$ over $PbCO_3$ in ground waters, accounts for failure of limonite derivatives of the pure smithsonite masses to be satisfactorily preserved in leached outcrops. Whatever the cause or causes, the fact of the poor preservation is established.

CHEMICAL CONSIDERATIONS.

Discussion of the chemistry of galena and sphalerite oxidation was given at length in the original paper. Inferences drawn were based largely upon conditions required to satisfy field observations.

Since then Anderson has confirmed those inferences in their main essentials by detailed microscopic work. His papers[1] are noteworthy contributions to the discussion.

ORIGIN OF THE LIMONITE PRODUCTS AND PATTERNS.

Previous papers have pointed out that the shape or pattern of cellular boxwork and sponge is governed by the cleavage, fracture, or crystal pattern of the unoxidized iron-yielding mass; and that such boxwork or sponge pattern is derived from deposition of limonitic jasper along the cleavage or fracture planes, or around crystal boundaries, during incipient oxidation. This explains why cellular boxwork or sponge so faithfully depicts the leached mineral.

The iron and silica that enter into the limonitic jasper of which boxwork or sponge is composed, are derived in large part from iron and silica imported by ground waters during the oxidation,

[1] *Op. cit.*

and only to a minor extent from the oxidizing cleavage or fracture plane area itself. Low solubility of limonitic jasper in acid and in bicarbonate solutions explains preservation of much of this cellular boxwork or sponge through subsequent oxidation processes.

Subsequent to formation of the boxwork or sponge at a given point, the residual sulphide or other mineral particle within the cell undergoes either slow or rapid oxidation. Where the sulphide or other mineral is readily soluble, as with sphalerite (or the solution highly acid, as with pyrite), most though rarely all of the oxidation products are carried in solution out of the cell, and in some cases completely out of the sulphide mass involved. In such case, where the sulphide is sphalerite, the final cellular product is left largely or wholly empty, and at most only the limonite grains, rosettes, and the small, irregular projections already discussed, remain as coatings upon the cell walls.

Where the sulphide or other mineral is not readily soluble, as with galena, anglesite, and cerussite, a much slower and often a pseudomorphic replacement of the minerals by limonite takes place. This produces the partially sintered limonite crusts characteristic of cerussite oxidation, and the relief limonite characteristic of anglesite oxidation. Either fills to an appreciable extent the cellular or sponge structure derived from, or the space formerly occupied by, the lead minerals, as illustrated in Fig. 1. The minutely thin cellular sponge of lead derivation at Eureka and Ely (Nevada), with its frequent though not invariable empty cellular spaces, constitutes an exception that has not thus far been satisfactorily accounted for.

The above products, being precipitated at the point from which the lead and zinc minerals were leached, are indigenous.

Limonite moss, on the other hand, being of stalactitic growth, is generally precipitated from a few millimeters to several centimeters from the point where the parent zinc mineral went into solution. It therefore usually occurs as a transported limonite product.

Again, limonite moss and the fluted columnar stalactitic structures of pyrite derivation, although they may be indigenous

or transported, generally are precipitated at a considerable distance—upwards of several inches or several feet—from the point of origin, and may be precipitated several miles from such point. The products, therefore, commonly occur also as exotic limonite, and their particular route and point of origin may be difficult to trace.

The minute microscopic space occupied by cleavage planes in ordinary galena deposits doubtless accounts in large part for the characteristically thin wall in cellular structures of galena derivation. Low solubility of adjacent galena while the boxwork is being formed, is in part also responsible. Possible greater thickness of cleavage or fracture planes in some instances, and more ready solubility of the sulphide or other mineral in most instances, is thought to account for the thicker walls of cellular structures derived from such minerals as sphalerite, chalcopyrite, bornite, etc.

A point not yet satisfactorily explained is the double (occasionally triple) parallel thin walls, with empty space between, that constitute the main ribwork of the diamond-mesh structure. We have evolved several hypotheses, based upon microscopic examination of the product during its incipient formative stages, to explain the condition, but none is wholly satisfying.

Special points noted in field observation of oxidizing lead minerals are:

1. "Cleavage" boxwork is the predominant cellular product where oxidation of the orthodox, symmetrically deposited, "cubic" galena has taken place.

2. Diamond-mesh boxwork is the predominant cellular product where oxidation of "steel" galena has taken place. It does not occur importantly in Mississippi Valley deposits. "Cleavage" boxwork, however, is prominent in most "steel" galena districts.

3. Cellular sponge of galena derivation occurs most commonly in deposits possessing a granular to semi-granular texture, as where fine to medium-grained schist or sedimentary beds have been replaced by galena.

Special points noted in field observations of oxidizing zinc minerals are:

1. Cellular sponge of zinc derivation most commonly occurs in deposits of the horizon zonally well below the top of intrusive stocks, or well down upon batholithic masses, as at Hanover (New Mexico).

2. The more angular cellular boxworks of zinc derivation commonly occur in deposits that are zonally near, or well above, the tops of intrusive stocks, as at the Ground Hog mine several miles from the Hanover batholith, or at the Golconda mine near Chloride, Arizona.

3. Both the cellular boxworks and the sponge structures of sphalerite derivation, as ordinarily found in the field, are patterned more closely after fracture than after cleavage or crystal form, though they do not follow fracture patterns exclusively.

4. Fracture pattern in the case of angular boxwork commonly conforms closely with the predominantly regular and sustained fissure and fracture systems of the country rock in deposits belonging to Lindgren's mesothermal and lower epithermal classifications,[4] or to Graton's mesothermal and leptothermal classifications;[5] and in the case of cellular sponge, conforms closely with the much more irregular fracture pattern of the country rock in deposits belonging to Lindgren's hypothermal and related pyrometasomatic classifications.

This circumstance has been used in the past to guide the search for "key" limonite types in zinc-bearing districts new to us. In part, however, the shape of the cellular structures is modified (1) by local divergencies from normal fracturing both for a given district and for individual ore bodies within a district, (2) by stresses set up within the primary ore body during cooling, and (3) (to a lesser extent) by sphalerite cleavage and crystal form.

The fracture patterns of certain other primary sulphides, notably chalcopyrite, have not been found to conform as closely as those of sphalerite to the district's regional fracture habit;[6]

[4] See the respective chapter headings in Lingren's "Mineral Deposits."

[5] See p. 536, ECON. GEOL., vol. 28, 1933.

[6] The case of cellular sponge of galena derivation, which is an apparent exception to the zonal fracture rule, can be explained through the fact that this sponge constitutes a broken replica of galena which to the unaided eye appears granular or

and there exists as yet no sound basis for determining how serviceable in general practice this correspondence may prove to be. It is held to be a partial explanation for the circumstance that in one district a given limonite type may be dominant almost to the exclusion of another type which in turn predominates in some other district.

SUMMARY

"Cleavage" boxwork and "partially sintered" limonite crusts have been confirmed as the principal identifiers of lead minerals in leached outcrops. The former is a cellular product patterned after galena's cubic cleavage, but usually poorly preserved. The latter is largely a pseudomorphic replacement of cerussite.

Additional limonite derivatives from galena are diamond-mesh and pyramidal boxworks. The former exhibits an unsymmetrical diamond-mesh pattern, with closely spaced, rigidly parallel ribs of very thin limonitic jasper, constituting the boxwork's major structure. It is derived from "steel" galena. The latter comprises a slender boxwork structure of step-pyramid pattern, as the pseudomorphic replacement in successively upward retreating stages of the more orthodox cubic cleavage type of galena.

Cellular sponge, composed of a confused spongelike structure that commonly emerges imperfectly from masses of the partially sintered limonite crusts, is found, under high magnifications ($\times$ 20 to 30), to consist of small, poorly developed, interlocking limonite boxes irregularly patterned after galena's cubic cleavage. It is a common derivative of galena that had pseudomorphically replaced schist or sedimentary beds other than limestone.

Relief limonite is a pulverulent product that commonly contains "ghosts" of cellular derivatives of lead minerals; but which, without such cellular derivatives, often cannot be differentiated from limonite of epidote, chlorite, or other unrelated origin. It

semi-granular in form; and that under high magnification the sponge resolves itself largely into minute, imperfectly joined, interlocking "cubic" boxes of limonitic jasper. Further field observation and further microscopic work may resolve the apparent inconsistencies of certain other sulphides which now seem to contradict the close correspondence in fracture patterns exhibited by sphalerite.

is derived chiefly from anglesite, and in most districts is quantitatively much less abundant than the cerussite-derived, partially sintered limonite crusts.

Cellular boxworks and cellular sponge have been confirmed as the principal limonite derivatives of sphalerite. Study of many specimens suggests that they are patterned more after a given sphalerite deposit's fracture system than after a specific cleavage form or crystal structure, though exceptions exist.

An additional limonite derivative from sphalerite is limonite moss. It occurs as long, loosely interconnected flakes and shreds of limonite, somewhat resembling shredded wheat biscuit but of more slender structure and of darker color, that locally fill and overrun the cellular limonite products of sphalerite derivation much as Spanish moss overruns and locally masks the limbs and foliage of trees. Being stalactitic, it represents a transported or exotic limonite, rather than the indigenous type to which belong the other sphalerite and galena-derived limonites described.

Smithsonite-derived limonite corresponding with the cerussite-derived, partially sintered limonite crusts, has not been identified as a standard type, although in individual districts a characteristic, poorly preserved product has been distinguished. Both as a parent mineral, and in changing to limonite, smithsonite often preserves its coherence less rigidly than does cerussite. Probably in part because of this fact, and in part because of its more ready solubility in ground waters, smithsonite rarely yields a well preserved pseudomorphic limonite product.

Data are presented which suggest that the patterns of sphalerite-derived cellular boxwork and sponge bear close relationship to a district's regional fracture pattern, as exemplified in Lindgren's hypothermal, mesothermal, and lower epithermal zones of mineralization. The check with cellular limonite derivatives of several other sulphides is less convincing, and more field observations and microscopic work are needed before a firm opinion in this matter may be offered.

MOUNT ISA MINES LIMITED,
MOUNT ISA, QUEENSLAND.

SILVER–TETRAHEDRITE RELATIONSHIP IN THE COEUR D'ALENE DISTRICT, IDAHO.

H. V. WARREN.

INTRODUCTION.

It has been generally accepted that a portion of the silver found in the Coeur d'Alene district is due to tetrahedrite. In this paper, assays of some tetrahedrite are given, and the proportion of the silver due to galena and to tetrahedrite is roughly determined.

Acknowledgments.—The general geology of the Coeur D'Alene mining district has been adequately dealt with by Ransome and Calkins,[1] and by Umpleby and Jones,[2] and frequent references to their work will be found in this paper.

I wish to thank most heartily Messrs. Stanley A. Easton and U. E. Brown of the Bunker Hill and Sullivan Mining and Concentrating Co., James F. McCarthy and L. E. Hanley of the Hecla Mining Co., C. E. Wethered and H. G. Washburn of the Federal Mining and Smelting Co., and R. E. Hooper of the Crescent Mine, for their ready assistance and co-operation.

Most of the work was done at the California Institute of Technology. The analytical work was done by Rodger W. Loofbourow at the University of Utah, working co-operatively with the Commonwealth Fund.

I also wish to thank Dr. F. L. Ransome and Mr. Engel of the California Institute of Technology for their invaluable help, advice, and criticism in the preparation of these notes, which will eventually be incorporated into a paper dealing with the occurrence and distribution of the precious metals in a number of important base metal mines in the Western United States.

[1] Ransome, F. L., and Calkins, F. C.: The Geology and Ore Deposits of the Coeur d'Alene District, Idaho. U. S. Geol. Survey Prof. Paper 62, 1908, 203 pp.

[2] Umpleby, J. B., and Jones, E. L.: Geology and Ore Deposits of Shoshone County, Idaho. U. S. Geol. Survey Bull. 732, 1923, 156 pp.

SILVER LEAD RATIO.

F. L. Ransome [3] showed that for a period of many years during the district's early days the silver content of the ore averaged about 0.60 ounces of silver per percent of lead. Examination of more recent data shows that this figure has remained remarkably constant. However, in a few mines in the district (*e.g.* the Crescent), the silver content is as much as 67 ounces per percent of lead, thereby considerably raising the average. Consequently, it was deemed advisable to ascertain the relationship between the silver and lead in the larger mines in which the silver ratio was considerably lower.

Joseph B. Umpleby [4] gives figures relative to the production of several mines from the commencement of their operation until 1915. From these figures, it can be seen that the silver-lead ratio varies considerably, not only between different mines but also in the annual production of a particular mine.

The silver-lead ratio for the Bunker Hill and Sullivan mine has varied from 0.26 in the early days of the mine up to about 0.40 in the second decade of this century.[5] According to R. S. Handy,[6] the West mill, which serves the Bunker Hill Mine, and the South Mill, which serves the Star Mine, treated ores with silver ratios of 0.37 and 0.29 respectively during the last two or three years. From figures given by C. E. Wethered and Leo J. Coady,[7] it is known that the silver ratio at the Morning mine is approximately 0.48 at the present time. Thus, it is evident, first, that the silver ratio is not decreasing appreciably, and second, that the silver ratio in the large mines in the district varies between 0.30 and 0.50, the average being nearer the lower figure.

Furthermore, an examination of the ratios of concentration [8] shows that in the lead concentrates not only is the percentage of lead recovered higher than the percentage of silver recovered, but

[3] *Op. cit.*
[4] *Op. cit.*
[5] *Idem.*
[6] U. S. Bureau of Mines, Information Circular 6314.
[7] U. S. Bureau of Mines, Information Circular 6238.
[8] References (1), (2) and (6).

also this disproportionate recovery is itself variable, showing that the galena is not directly responsible for all the silver found in these mines.

SILVER-GALENA RATIO.

Galena was taken from three different places in the Bunker Hill and Sullivan Mine. It was crushed, screened, and classified. Then a selection was made by hand of the cleanest looking galena, and this selected material was assayed. The assays showed that the galena carried silver in surprisingly similar amounts, the three assays not varying by more than .0035 per cent. of silver, the limits being .0845 oz. and .088 oz. of silver per ton: this corresponds to a silver ratio of approximately .306.

Polished sections were made of a number of specimens from the Hecla and Bunker Hill and Sullivan mines, and although in none of the samples of the material which was assayed can any tetrahedrite be seen without etching, yet in about one sample in three, tetrahedrite can be readily seen on the polished surfaces with the aid of a hand lens.

F. L. Ransome [9] mentioned in his paper that "steel" galena was, in this district, reputedly rich in silver, and it was significant that tetrahedrite was found most abundantly in this variety of galena.

An analysis was then made of galena from the Sunshine Mine, which is known to contain much tetrahedrite and to be rich in silver. Although the galena appeared megascopically to be free from tetrahedrite, the assay showed 0.15 per cent. of silver, all of which could be explained as being due to tetrahedrite because the assay revealed the presence of copper, arsenic, and antimony in the galena.

A polished section of galena from the Crescent Mine was also examined, and this section contained abundant inclusions of tetrahedrite, although an inspection of the hand specimen of galena did not reveal a trace of that mineral.

The significant point arising from this discussion is the fact that, except in mines where the silver ratio is below 0.30, the

[9] *Op. cit.*

galena does not carry sufficient silver to account for all the silver which is produced in these mines.

SILVER-TETRAHEDRITE RATIO.

Through the courtesy of Mr. H. L. Goodwin, who presented me with some rich samples of ore from the Sunshine Mine near Kellogg, it was possible to pick out two samples of relatively pure tetrahedrite for analysis. The results were as follows:

	A	*B*
Sulphur	24.16	24.44
Arsenic	10.13	8.59
Antimony	22.36	22.36
Copper	29.10	29.10
Silver	3.95	6.15
Zinc	5.09	3.56
Iron	5.50	5.50
	100.29	99.70

Some polished sections of this tetrahedrite were examined, and these showed that small amounts of blende and siderite had unavoidably been included in the samples. The samples themselves were so small that it is not possible to state categorically that all the zinc and iron in the assay are due to impurities of blende and siderite, but nevertheless such does appear to be the case. The analysis of the tetrahedrite would be as follows, after removing sulphur in sufficient quantities to combine with the zinc:

	A	*B*
Sulphur	21.67	22.70
Arsenic	10.13	8.59
Antimony	22.36	22.36
Copper	29.10	29.10
Silver	3.95	6.15
	87.21	88.90

After recalculating to 100 per cent the assay is then brought to atomic proportions:

	A			*B*		
Sulphur	24.85	÷ 32.0	.78	25.54	÷ 32.0	.79
Arsenic	11.62	÷ 75.0	.16	9.66	÷ 75.0	.13
Antimony	25.60	÷ 120.0	.21	25.12	÷ 120.0	.21
Copper	33.40	÷ 64.0	.52	32.77	÷ 64.0	.51
Silver	4.53	÷ 108.0	.04	6.91	÷ 108.0	.06
	100.00			100.00		

No legitimate juggling of these figures will provide a simple formula. If a little zinc is considered as belonging to the tetrahedrite, the formula becomes $Sb_2S_3 . 2Cu_2S$, some Cu_2S being replaced by 6(Cu Zn)S, silver replacing copper, and arsenic replacing antimony throughout.

I do not consider this conclusion satisfactory, but present it in view of a paper by Prior and Spencer,[10] who discuss a replacement of Cu_2S by 6(Fe Zn) in tetrahedrite. It is of interest to note that the formula of this tetrahedrite varies considerably from the type formula in that this Coeur d'Alene variety contains at the best only two molecules of Cu_2S, or its equivalent, instead of three or four, to one molecule of Sb_2S_3.

A detailed description of this and several other varieties of tetrahedrite occurring in the western United States will be presented in another paper.

What appears to be similar tetrahedrite to that which was analyzed occurs in many mines, and is presumably responsible for the bulk of the silver not accounted for by the galena, because no other primary silver mineral is found in appreciable quantities.

Waldschmidt [11] reports finding tetrahedrite and freibergite in the ores from several mines, but since he was able to separate them only by etching with nitric acid and potassium cyanide, there is a strong probability that these two minerals are one variety of an argentiferous tetrahedrite, since it is virtually impossible to separate tetrahedrite and freibergite except by chemical analyses. He was unable to have chemical analyses made owing to the smallness of the mineral grains, which in many cases were too small even to test for silver.[12]

[10] Prior, G. T., and Spencer, L. J.: The Identity of Binnite with Tetrahedrite; and the Chemical Composition of Fahlerz. Miner. Mag., vol. 12, p. 184, 1899.

[11] Waldschmidt, W. A.: Deformation in Ores, Coeur d'Alene District. Econ. Geol., vol. 20, p. 573, 1925.

[12] Subsequent to submitting this paper for publication, through the courtesy of Mr. R. S. Hooper (personal communication) the author obtained permission from Mr. Easton and Mr. Handy of the Bunker Hill and Sullivan Mining and Concentrating Company to quote the following assays of their company's various concentrates in support of the conclusions here given:

CONCLUSIONS.

Careful assays and examinations of galena and tetrahedrite from ores coming from both high and low grade silver mines bear out analytically what has been recognized in a general way for some time, namely, that the galena in the Coeur d'Alene district does not carry more than 0.30 ounces of silver in each percent of lead. This is not sufficient to account for the silver even in the deposits low in that metal. The remainder of the silver is contributed by argentiferous tetrahedrite, which is generally found to be older than the galena.

From 0 to 50 per cent. of the silver in the low silver deposits is contributed by tetrahedrite, from 5 to 40 per cent. being very common.

The fact that higher silver values are usually found in the "steel" galena, where tetrahedrite is also observed, suggests the possibility that the tetrahedrite is of secondary origin. No microscopic evidence was found to support this idea.

In view of the fact that only the tetrahedrite which could be seen without etching was considered and that undoubtedly some small particles would be missed owing to "smearing" of the galena during polishing, it is possible that the galena carries even less silver than has been stated, and tetrahedrite is correspondingly more important.

Thus, the greater proportional loss of silver relative to lead, in the lead concentrates, must be due almost entirely to a loss of tetrahedrite. Whether or not the saving of this tetrahedrite in the low silver deposits is metallurgically or economically feasible, I am not competent to say.

UNIVERSITY OF BRITISH COLUMBIA,
VANCOUVER, CANADA.

	Pb.	Ag.	Ratio
Jig Concentrates	47.48	18.18	.382 oz. Ag per % of Pb.
Table Concentrates	66.51	24.92	.374 " " " " " "
Flotation Concentrates ..	63.05	29.69	.471 " " " " " "
Zinc Concentrates	3.21	3.42	1.065 " " " " " "

These figures show clearly that galena is not responsible for all the silver which occurs in the Coeur d'Alene District.

THE BERYL–MOLYBDENITE DEPOSIT OF CHAFFEE COUNTY, COLORADO.

KENNETH K. LANDES.

INTEREST has recently been aroused in deposits of beryl because of the new use of beryllium as an alloy metal, particularly as an alloy with copper, to which it imparts unusual properties. In addition, the occurrence of beryl in a quartz vein is unusual. The writer believes that deposits of this type are formed by hydrothermal solutions of pegmatitic origin.

Location.—The beryl-molybdenite vein of central Chaffee County outcrops at an elevation of 12,500 feet on the north side of the headwaters-amphitheater of Brown's Creek, an eastward-flowing tributary of the Arkansas River. This deposit was worked for molybdenite in 1917 and 1918, but is now abandoned. Routes to the mine (known as the California Mine) are discussed by Worcester.[1] The writer visited the deposit in July, 1932, guided by Herman Schneider of Buena Vista.

Previous Investigations.—This deposit was briefly described by Crawford [2] in 1913, and a more complete report was published in 1919 by Worcester.[3] Hess [4] was the first (to the writer's knowledge) to mention the presence of beryl. An analysis of molybdite from this locality was published by Schaller [5] in 1911. Both Hess and Schaller refer to the deposit as near Hortense, which is a long-abandoned station on the D. & R. G. railroad near the mouth of Brown's Gulch.

1 Worcester, P. G.: Molybdenite Deposits of Colorado. Colorado Geol. Survey, Bull. 14, 1919.

2 Crawford, R. D.: Geology and Ore Deposits of the Monarch and Tomichi Districts, Colorado. Colorado Geol. Survey, Bull. 4, p. 279, 1913.

3 *Op. cit.*, pp. 34–38.

4 Hess, F. L.: Molybdenum. U. S. Geol. Survey, Mineral Resources, 1917, pt. 1, p. 912.

5 Schaller, W. T.: Mineralogical Notes, Series 1. U. S. Geol. Survey, Bull. 490, pp. 84–92, 1911.

More attention has been given in the literature to the occurrence of gemworthy aquamarines and crystals of phenacite and bertrandite in pegmatites that outcrop on the flanks and near the summit of Mount Antero.[6] Mount Antero lies a short distance northeast of the California Mine.

GEOLOGY AND MINERALOGY.

Description.—The country rock in the vicinity of the beryl-molybdenite vein is the Pomeroy quartz monzonite.[7] According to Crawford, the monzonite at the headwaters of Brown's Creek has been separated from a much larger mass in the northwest part of the Monarch district by intrusion of younger granite.[8] Both the Pomeroy quartz monzonite and the granite are post-Carboniferous and probably Tertiary. Specimens of the country rock collected from near the vicinity of the beryl-molybdenite vein were gray in color and finely granular. Both plagioclase and orthoclase feldspar are present.

The vein is about 2 feet wide where at present exposed. The dip is practically vertical. Small pockets containing quartz crystals, beryl, sericite, molybdenite, and molybdite are abundant. A few very small fragments of black tourmaline were also found. Brief descriptions of these minerals follow.

Quartz is by far the most abundant mineral in the vein. It ranges in color from nearly colorless through smoky to milky, the last named being the most common. The quartz is massive, except in the vugs, where clear or smoky terminated prismatic crystals occur. Embedded in the massive milky quartz are small prismatic crystals of beryl.

[6] Cross, R. G.: Notes on Aquamarine from Mt. Antero. Amer. Jour. Sci., (3) vol. 33, pp. 161–162, 1887; Smith, W. B.: Mineralogical Notes, 1, 2 and 3. Colorado Sci. Soc., Proc., vol. 2, pp. 177–179, 1887; Penfield, S. L.: Phenacite from Colorado. Amer. Jour. Sci., (3) vol. 33, pp. 131–134, 1887. Bertrandite from Mt. Antero. Amer. Jour. Sci., (3) vol. 36, pp. 52–55, 1888. Some Observations on the Beryllium Minerals from Mt. Antero. Amer. Jour. Sci., (3) vol. 40, pp. 488–491, 1890; Penfield, S. L., and Sperry, E. S.: Mineralogical Notes. Amer. Jour. Sci., (3) vol. 36, p. 32, 1888; Over, Edwin, Jr.: Mineral Localities of Colorado. Rocks and Minerals, vol. 3, pp. 110–111, 1928.

[7] Crawford, R. D.: *Op. cit.*, p. 279.

[8] Crawford, R. D.: *Op. cit.*, p. 79.

Beryl is fairly common. Most of it is green, although a few specimens are bluish. The locality has produced a few gem-worthy aquamarines. The largest crystal found by the writer measures 5 cm. in length by 3 cm. in diameter. The smallest beryls collected are less than 1 cm. in length by 1 to 2 mm. in diameter. One crystal is a nearly clear aquamarine measuring 36 by 18 mm. It is doubly terminated and exhibits prism, base and second order pyramid. The second order prism is very slightly developed. The beryls occur both completely embedded in massive quartz and partially embedded with the ends protruding into cavities.

The *mica* in the vein is sericite. It occurs in silver-colored scales and minute books. It is confined to vugs or cavities and is often found perched on quartz crystals.

Molybdenite occurs (1) in isolated patches which either coat the walls of the vugs or lie between crystals of quartz and beryl, and (2) in thin veins that cut massive quartz. The latter are composed exclusively of molybdenite and range in thickness from 1 to 3 mm. A few exceptionally high-grade masses of molybdenite were observed in the cavities and much larger masses were observed by Worcester. *Molybdite,* an oxidation product of molybdenite, occurs as a yellow powder and has, naturally, the same associations as molybdenite. In a few specimens the molybdenite has been entirely altered into molybdite. Molybdite is the only supergene mineral of importance in the vein.

Sequence of Mineralization.—The vein minerals were deposited in the following order: quartz (massive), beryl, quartz (crystals), mica, molybdenite, and molybdite (supergene). The solutions that brought in the beryl were capable of dissolving quartz, since vugs were formed in the massive milky quartz. Some of the beryl crystals completely replaced quartz; others replaced quartz at one end while the other end grew out into a cavity. Following the beryl deposition, the solutions again changed in their chemical character so that the quartz was no longer attacked. On the contrary, a second generation of quartz was deposited as euhedral or subhedral crystals in the cavities. Then the sericite was pre-

cipitated, likewise in the cavities and commonly on the faces of the second generation quartz crystals. The deposition of molybdenite closed the hypogene mineralization. Abundant evidence is present of the relatively late age of the molybdenite. It coats every other vein mineral, including sericite. It tends to fill in re-entrant angles between the vuggy crystals. In one specimen milky quartz has been etched to a furrowed surface and the furrows are partially filled with molybdenite.

Not enough tourmaline is present to place it in the sequence. It was undoubtedly early, however.

GENESIS OF DEPOSIT.

The quartz-beryl-molybdenite vein was deposited by ascending hydrothermal waters. The presence of beryl and tourmaline indicates that the solutions were of the high-temperature type. The ultimate source of the solutions was an acid magma, perhaps the granite magma which was intruded into the Pomeroy quartz monzonite. It is the belief of the writer, however, that a crystallizing pegmatite furnished the immediate source of the mineralizing solutions. This belief is based upon the presence of beryl among the constituents of the vein. Pegmatite is the typical habitat of beryl, where it may appear as a product of both magmatic crystallization and later hydrothermal activity. A pegmatite at Buckfield, Maine, contains two distinct types of beryl, one the common bluish green translucent variety, and the other a light-colored transparent beryl containing small amounts of caesium. The former crystallized during the primary solidification of the pegmatite, and the caesium beryl was deposited by later hydrothermal solutions that were given off by deeper-seated portions of the crystallizing pegmatite.[9] Such hydrothermal solutions of pegmatitic origin do not necessarily confine themselves to the pegmatite, but may travel out into the adjacent country rock.

Exceptionally, beryl is found in deposits other than pegmatites.

[9] Landes, Kenneth K.: The Paragenesis of the Granite Pegmatites of Central Maine. Amer. Miner., vol. 10, p. 374, 1925.

Examples are the emerald occurrences in schist,[10] the Muzo, Colombia, emerald-calcite veins,[11] and beryl-containing wolframite-quartz veins in Burma,[12] Tasmania,[13] and New South Wales.[14] But in most of these occurrences the investigators report the presence of pegmatites in the district and ascribe the origin of the beryl and associated minerals to deposition by pegmatitic solutions. Palache [15] has recently described pink beryl crystals that occur in cavities in rhyolite at Topaz Mt., Utah. The writer believes that minerals having this occurrence are formed through deposition by "fugitive" constituents of the solidifying lava and are analogous in origin to those found in pegmatites.

The beryllium-rich pegmatites of Mount Antero lie but a short distance from the Chaffee County quartz-beryl vein and probably belong to the same period of mineralization. Apparently beryllium was present in unusual proportions in the original granitic magma and became concentrated in the resulting pegmatite magma. The latter was injected into the country rock in the vicinity of Mount Antero, forming pegmatite dikes. Hydrothermal solutions, which were likewise rich in beryllium, were given off during the crystallization of the pegmatites, and the

[10] Fersmann, A.: Geochemische Migration der Elemente. Abh. prakt. Geol., Bd. 18 and 19, 1929; cited by Lindgren, W.: Mineral Deposits, (1933) p. 766. Aitkens, Irene: Emeralds. U. S. Bur. Mines, Inf. Circ. 6459, p. 6, 1931; Beryllium and Beryl. Imperial Institute, 1931, p. 14. Le Grange, J. M.: The Barbara Beryls, etc. Trans. Geol. Soc. So. Africa, vol. 32 (for 1929), p. 13, 1930. Spence, Hugh S.: Notes on Beryllium and Beryl. Canadian Dept. of Mines, Mines Branch, Mem. 40, p. 5, 1930.

[11] Pogue, J. E.: The Emerald Deposits of Muzo, Colombia. Trans. Amer. Inst. Min. Eng., vol. 55, pp. 910–934, 1917; Ball. S. H.: The Geologic and Geographic Distribution of Precious Stones. ECON. GEOL., vol. 17, p. 591, 1922.

[12] Brown, J. C., and Heron, A. M.: The Distribution of Ores of Tungsten and Tin in Burma. Records, Geol. Survey of India, vol. 50, pt. 2, pp. 101–121, 1919.

[13] Rastall, R. H.: Molybdenum Ores. Imperial Institute Monograph, 1920, p. 52; Reid, A. McIntosh: The Mining Fields of Morina, Mt. Claude, and Lorinna. Tasmania Geol. Surv., Bull. 29, pp. 52–54, 1919.

[14] Conder, Hartwell: The Wolfram Deposits of New England. Mining Jour., vol. 78, p. 170, 1905.

[15] Palache, Charles: Minerals from Topaz Mt., Utah. Amer. Miner., vol. 19, pp. 14–15, 1934.

solutions from one such pegmatite produced the beryl-molybdenite-quartz vein.

CONCLUSIONS.

The writer believes that the relationship between beryl and pegmatite is so close that one is justified in assuming that beryl-containing deposits have been formed by pegmatitic solutions. The quartz-molybdenite-beryl vein of Chaffee County, Colorado, which occurs in a region of granite and pegmatite intrusion, is thought to have been deposited by hydrothermal solutions escaping from a deeper solidifying pegmatite.

If these conclusions are correct, quartz veins containing beryl may be looked upon as a link connecting pegmatites with normal quartz veins.

ACKNOWLEDGMENTS.

The field work was made possible through a grant from the Elizabeth Thompson Science Fund. The writer wishes to express his gratitude to this organization for its assistance. Mr A. L. Morrow accompanied the writer in the field and the aid which he rendered is much appreciated. Prof. G. L. Knight read a preliminary draft of the manuscript and made a number of helpful suggestions which have been followed in preparing the final copy.

UNIVERSITY OF KANSAS,
LAWRENCE, KANSAS.

DISCUSSION AND COMMUNICATIONS

PROBLEM OF SERPENTINIZATION.

Sir: Comment by Mr. Dresser [1] would lead the readers of this Journal to believe that " the conclusions of Keith and Bain [2] were drawn essentially from a study of ' slip-fiber ' deposits of Lowell Mountain, Vermont." The latter authors drew most of their conclusions from cross-fiber veins, and illustrated typical critical examples in figures 7, 8 and 9 (p. 184) and figure 11 (p. 186). Actually, no deposits of asbestos or ultrabasic rocks occur in Lowell Mountain (or Mountains); the nearest occurrences mentioned by Keith and Bain are in Belvidere Mountain, where the Vermont Asbestos Corporation has developed a large body of slip-fiber on the south slope, and the Gallagher mine opened up a zone of cross-fiber veins at the eastern base. Limited ratio of width of serpentinization to width of cross-fiber vein, as observed by Dresser, is not evident in any Vermont cross-fiber deposits; representative variation of the ratio is given in tables by Keith (pp. 181–182).

GEO. W. BAIN.

AMHERST COLLEGE,
AMHERST, MASS.

1 Dresser, J. A.: The Problem of Serpentinization. ECON. GEOL., vol. 29, p. 306, 1934.

2 Keith, S. B., and Bain, G. W.: Chrysotile Asbestos. ECON. GEOL., vol. 27, pp. 169–188, 1932.

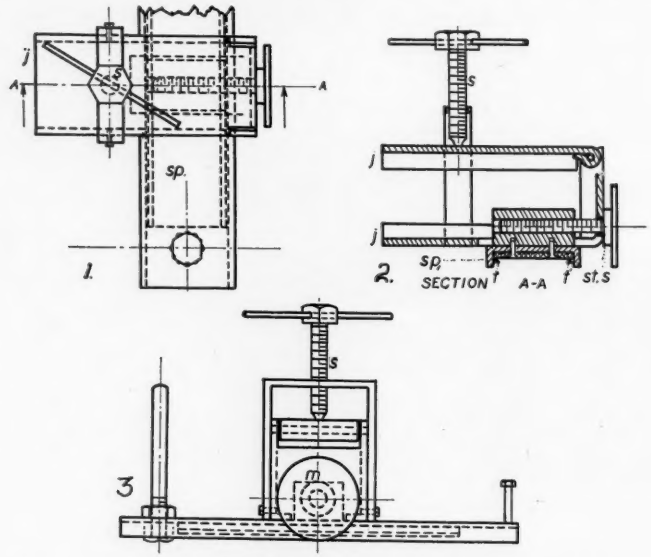
A HOLDER FOR A DIAMOND SAW.

A SIMPLE diamond saw which can be used for cutting rock sections has been described by Vanderwilt,[1] but he makes no mention of a holder and this is necessary for efficient operation of

1 Vanderwilt, John: A Simple Diamond Saw. ECON. GEOL., vol. 25, No. 2, March–April, 1930, pp. 222–225.

the saw. A saw constructed according to Vanderwilt's description has been in operation in our laboratory for several years and the holder described here was designed and built by a machinist and advanced students under the direction of the writer.

An electric motor bearing a copper disc, as described by Vanderwilt, is mounted on an I-beam with the shaft parallel to the axis of the beam. About two inches from the end of the shaft, a metal block is fastened firmly to the I-beam with its axis parallel to the plane of the saw. The top of this block is grooved to receive the tongued edges of the sliding plate *sp* (Figs. 1 and 2).



FIGS. 1–3. (1) Plan (from above). (2) Section. (3) Side view.

This is a metal plate of the same length as the metal block, upon which it is held by the tongued edges *tt'* (Fig. 2) so that it slides back and forth parallel to the saw. A cord with a suitable weight attached to it passes over a pulley on an arm on the I-beam

and is attached to the end of the sliding plate. This serves to keep the rock pressed against the saw with correct force.

The holder is composed of two jaws *jj'* (Fig. 2). In the lower jaw of the holder a slit is cut parallel to its axis, through which the bolts pass by which the jaw is fastened to the sliding plate. The jaw can thus be moved forward and backward in a direction at right angles to the movement of the sliding plate and plane of the saw. This movement is controlled by the set screw, *st s* (Fig. 2). This screw has a very fine thread so that the jaw can be moved a definite short distance.

The jaws are clamped together by the large screw *s* (Fig. 2). The rock from which the section is to be cut is placed between two pieces of wood of suitable size, and the set screw is adjusted until the rock is brought into proper position for cutting. The motor is then started and the sliding plate moved forward until the rock is in contact with the saw. After the rock is sawed through, the sliding plate is pulled back, the rock is moved a short distance past the plane of the saw by means of the set screw *st s*, and is again brought in contact with the saw by moving the sliding plate along the block toward the saw. By this means a cut parallel to the first cut is made.

With the above-described apparatus it is easily possible to cut rock slices one millimeter or less in thickness. This greatly reduces the time of making thin sections.

The apparatus can be made in any machine shop and is relatively inexpensive.

LEROY T. PATTON.

DEPARTMENT OF GEOLOGY,
TEXAS TECHNOLOGICAL COLLEGE,
LUBBOCK, TEXAS.

REVIEWS

Die Bodenschätze des Staates Minas Geraes (Brasilien.) By Dr. B. v. Freyberg. Pp. xi + 403, figs. 73, pls. 12. E. Schweitzerbart'sche Verlagsbuchhandlung, Stuttgart, 1934. Price, 54 M.

In this journal (Vol. 28, p. 188, 1933) attention was called to the author's treatise on the general geology of the State of Minas Geraes. In that volume he gave an outline of the State's geology. In the present volume he discusses, in as full detail as is now possible, its ore and mineral deposits. He collects all the trustworthy information on the subject that has been published during the past century and adds to this the results of his own observations made during his extensive travels over the territory between 1925 and 1930. He thus furnishes us with the only comprehensive account of the mineral resources of the State that is available.

The volume is introduced by a chapter of 45 pages on the State's general topographic, geologic and cultural features. This constitutes Part I.

Part II, which includes all the remainder of the book, deals with deposits of gold, platinum, manganese, iron, nickel, bismuth, lead, zinc, copper, and cinnabar, radium and zircon ores, and deposits of sulphur, pyrite, bauxite, diamond, topaz, beryl, tourmaline, semiprecious stones, quartz, monazite, mica, kaolin, clay, soapstone, asbestos, talc, pigments, barite, limestone, saltpeter, alkali-carbonates, glauber-salt, coal and graphite.

Reference is also made to tin, tungsten, antimony and cobalt ores, and molybdenite, all of which are present in the State, but so far as now known, not in commercial quantities; and to the many mineral and hot springs and baths existing within its area.

The most comprehensive discussions deal with the gold, manganese and iron ores, the diamond and monazite deposits and those of the precious stones. In all cases not only are their occurrences described but also there is a summary of the views of various geologists as to the sources of their material, and prefixed to the discussion of each deposit is a bibliographic list of all publications relating to them. For instance, the bibliography for manganese contains 37, that of precious and semiprecious stones 126, and that for diamond 129 entries.

Concluding the volume is a 16 page, double-column, place index.

The book should be of great value to those interested in the development of the mineral resources in this, the most productive portion of Brazil.

W. S. BAYLEY.

The Chemistry of Solids. By CECIL H. DESCH. Pp. 213, figs. 55. Cornell Univ. Press, Ithaca, N. Y., 1934. Price, $2.50.

This volume represents a series of lectures delivered at Cornell by Professor Desch, of the National Physical Laboratory, England, formerly professor of metallurgy at the University of Sheffield. It combines phases of modern crystallography, metallurgy, micro-chemistry, and physical chemistry, and therefore is of interest to all economic geologists. The following subjects are covered: constitution of solids; growth, adsorption, habit, boundaries, and mosaic structure of crystals; etch figures; surface films and passivity; abrasion and corrosion-fatigue; diffusion in solids; Widmanstätten and martensite structure; ageing and hardening of alloys; intermetallic compounds; chemical changes in solids; layered lattice, and fiber structure.

The volume is clearly written, well illustrated by many photomicrographs and composition diagrams, and contains much material of value to chemists and geologists.

Angewandte Geophysik für Bergleute und Geologen. By H. REICH. Teil II. Pp. 153, illus. 73. Akad. Verlagsgesellschaft M. B. H., Leipzig, 1934. Price, 10.60 M.

The second part of Dr. Reich's little book on the various uses of geophysical methods in geological investigations (see this Journal, Vol. 28, p. 700) deals with the physical properties of different kinds of rocks and the methods of determining them. This is followed by very clear directions for recognizing the existence of magnetic substances underground by (*a*) magnetic, (*b*) electrical and (*c*) gravimetric methods. In each case explicit descriptions for prosecuting each type of investigation are given and each method is illustrated by an example in which the method has been used. Under each heading is a short list of papers dealing with the employment of the method in the working-out of a special district.

In a separate section is a discussion of the use of the methods in the search for kaolin, clay, sand, sulphides and other non-magnetic substances, including water.

The treatise (including both parts I and II) although small, contains all the information needed in the solution of the less complicated problems that may be faced by the field geologist.

W. S. BAYLEY

The Mineral Industry during 1933. Edited by G. A. ROUSH, with 33 contributors. Vol. 42, pp. 745. McGraw-Hill Book Co., New York, 1934. Price, $12.00.

This new volume, the 21st under Mr. Roush's editorship, is of more than usual interest because of the changed conditions of the metal industry, particularly of gold and silver. After a mention of foreign coins, State surveys, trade associations, and professional organizations, it deals, as usual, with each important mineral substance. Particularly pointed in this volume are the general considerations of gold and silver, copper, tin, lead and zinc, with a general review of these (and others) during the period of the editor's tenure.

The Mineral Industry continues to be a necessary reference for all those interested in its statistics, technology, and trade.

BOOKS RECEIVED.

DAVID GALLAGHER.

Geologic Map of the Kettleman Hills, California. (Advance edition.) U. S. Geol. Survey, Washington, D. C. Scale 1:31680; structure contours 100 ft. interval; size 41″ x 53″. A noteworthy structure map of an unusual structure; shows entire anticline and amazing parquetry of crest faults; four cross sections and four geologic columns.

The Wonderlode of Silver and Gold. MIRIAM MICHELSON. Pp. 347. Stratford Co., Boston, 1934. $2.50. A book of romance and adventure, based on fact, with considerable history and biography, of the early days of Comstock Lode and Virginia City.

Canada Dep't Mines, Annual Report, Year ending March 31, 1933. W. A. GORDON. Pp. 43. Ottawa, 1933. Administrative report and account of activities.

Oil and Gas in Western Canada. 2d Ed. G. S. HUME. Pp. 359, figs. 26. Canada Geol. Surv., Econ. Geol. Ser. No. 5. Ottawa, 1933. 75c. Synopsis of oil geology; descriptions of the oil and gas occurrences in Western Canada, replete with well logs.

Geochemische Migration der Elemente. A. FERSMANN. Pp. 116, figs. 22, pls. 4. Abhandl. zur prakt. Geologie und Bergwirtschaftslehre, Bd. 18. Wilhelm Knapp, Halle (Saale), 1929. Pt. I: Die Aufgaben der topomineralogischen Forschung; Agpaitische Pegmatite der Halbinsel Kola; Smargdgruben im Ural. Bd. 19. Pt. II. Pp. 86, figs. 20, pls. 8. (1) Die Uran-Vanadium-Grube Tuja-Mujun in Turkestan. (2) Die Schwefelhügel in der Mittelasiatischen Wüste Karakumy.

Geochemie der Erdöllagerstätten. K. KREJCI-GRAF. Pp. 54, figs. 12. Abhandl. zur prakt. Geologie und Bergwirtschaftslehre, Bd. 20. Wilhelm Knapp, Halle (Saale), 1930.

Die Goldlagerstätte des Eisenbergs bei Corbach. P. RAMDOHR. Pp. 39, pls. 8. Abhandl. zur prakt. Geologie und Bergwirtschaftslehre, Bd. 21. Wilhelm Knapp, Halle (Saale), 1932.

Mineral Resources of the United States, 1931. Part II. Nonmetals. O. E. KIESSLING. Pp. 675. U. S. Bur. Mines. Washington, 1933. $1.

Geological Map of Malaya, 1930. F. M. S. Geol. Surv. In color. Scale 12 miles to an inch, size about 2 x 3 ft.

Imperial Institute, Ann. Rpt. 1933. SIR WILLIAM FURSE. Pp. 55. London, 1934. 2 s. Administrative report and account of activities.

Investigations of Fuels and Fuel Testing, 1932. Pp. 155, pls. 7, figs. 8. Canada Dept. Mines, Mines Branch, No. 737. Ottawa, 1934. Contains nine papers.

Geology of the Prestea Goldfield. W. G. G. COOPER. Pp. 20, pls. 8, geol. map. Gold Coast Geol. Surv. Mem. 3. London, 1934. 5/–. Gold quartz veins in isoclinally folded and thrusted pre-Cambrian rocks.

Geologic Map of the Appalachian Valley of Virginia with Explanatory Text. C. BUTTS. Pp. 56. Virginia Geol. Surv. Bull. 42. University, 1933. In color, scale 1 : 250,000, size about 4 x 5 ft. No contour lines.

Limestones of Canada, Their Occurrence and Characteristics. Part II, Maritime Provinces. M. F. GOUDGE. Pp. 186, pls. 29, figs. 12, maps 2. Canada Dept. Mines, Mines Branch, No. 742. Ottawa, 1934. 50c.

Ontario Dept. Mines, 42d Ann. Rpt. Vol. XLII, 1933. Toronto, 1934. Pt. IV, Geology of the Manitou-Stormy Lakes Area, J. E. THOMSON; Geology of the Kakagi Lake Area, E. M. BURWASH. Pt. V, Natural Gas and Petroleum in 1932, R. B. HARKNESS. Pt. VI, Geology of the Pashkokogan-Misehkow Area, W. S. DYER; Geology of the Shabumeni-Birch Lakes Area, G. D. FURSE.

Brown Iron Ores of the Western Highland Rim, Tennessee. E. F. BURCHARD *et al.* Pp. 227, pls. 33, figs. 21. Tenn. Dept. Educ., Div. of Geol. Bull. 39. Nashville, 1934. Description of occurrences by counties.

Mount Eielson District, Alaska. J. C. REED. Pp. 56, pls. 4, figs. 5. U. S. Geol. Surv. Bull. 849–D. Washington, 1933. 25c. Regional geology, and descriptions of the mines. High-temperature lead, zinc and copper replacements of Paleozoic limestones contiguous to late Mesozoic granodiorite stock.

Copies of books mentioned under "Reviews" or under our "New Book List" (see advertisement page) may be purchased through our Journal Bookshop by writing to W. S. Bayley, University of Illinois, Urbana, Ill.

SCIENTIFIC NOTES AND NEWS

Frank L. Hess, chief of Rare Metals and Nonmetals Division, U. S. Bureau of Mines, recently returned from a visit to Mexico.

J. F. Wright has left the Canadian Geological Survey and will engage in private consulting practice.

John Wellington Finch, of the State Geological Survey at Moscow, Idaho, has succeeded Scott Turner as director of the U. S. Bureau of Mines.

W. C. Douglass, recently with the Auburn Chicago Mining Company, Penryn, Calif., is now general manager of the Kelowna Exploration Company, which has taken over the Nickel Plate mine, British Columbia, and is getting it ready for operation.

E. N. Pennebaker, of Consolidated Coppermines, Kimberley, Nevada, is president of the recently organized White Pine County Prospectors' Association.

Percy G. Dobson is conducting diamond drilling exploration at the Cariboo Amelia mine, Camp McKinney, B. C., Canada, which was producing up to 1900, when operations were discontinued on account of faulting which cut off the ore bodies.

George F. Kay, state geologist of Iowa and head of the Department of Geology in Iowa University, has resigned but will retain his professorship in geology, also his duties as dean of the College of Liberal Arts.

E. L. Bruce, of Queen's University, Kingston, Ontario, has been engaged during the summer in exploring the Little Long Lac area north of Lake Superior for the Ontario Department of Mines.

S. A. Thompson is now chief geologist for the Magnolia Petroleum Co. of Dallas, Texas.

Frederick G. Clapp recently returned to New York after an extended tour through the countries of western Asia.

Sir Edgeworth David, well known as a geologist and writer, died on August 28 at Sydney, Australia, aged 76.

Charles L. Dake, professor of geology in the School of Mines and Metallurgy at the University of Missouri, died at Denver, Colorado, on September 3.

The recently published 20-volume index (336 pages) of ECONOMIC GEOLOGY for 1905 to 1925, compiled by J. M. Nickles, may be obtained for $3.00 from W. S. Bayley, University of Illinois, Urbana, Ill.